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DEVELOPMENT OF SILOXANE-CONTAINING EPOXY
POLYMERS FOR ELECTRICAL CIRCUIT
EMBEDMENT APPLICATIONS

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FOR ELECTRICAL CIRCUIT EMBEDMENT APPLICATIONS

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Huntsville, Alabama

ABSTRACT

This report describes the synthesis of seven epoxy polymer precursors which contain the siloxane linkage in varying structural arrangements, and the polymerization of these materials with aromatic diamines. The polymers prepared from such intermediates have utility as embedment compounds for electrical circuits. Seven epoxy intermediates were prepared, characterized, and subsequently polymerized into solid, thermosetting materials for which dielectric property data were obtained. Dielectric constants as low as 3.1 at one kilocycle were measured for polymers prepared from polymerization of 1,9-bis(p-(2,3-epoxypropyl)phenyl)decamethylpentasiloxane with 1,4-bis(p-aminophenoxy)tetramethyldisiloxane, whereas polymers derived from 1,4-bis((p-(2,3-epoxypropyl)phenyl)dimethylsiloxy)dimethylsilyl)benzene and the same diamine were characterized by slightly higher dielectric constants and a high degree of toughness.

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PROPULSION AND VEHICLE ENGINEERING LABORATORY
RESEARCH AND DEVELOPMENT OPERATIONS

TABLE OF CONTENTS

	Page
SUMMARY.....	1
INTRODUCTION.....	1
DISCUSSION	2
Formation of Polymer Intermediates.....	2
Aminosilane-Silanol Condensations.....	5
Epoxidations.....	8
Curing Agents.....	11
Polymerizations.....	12
EXPERIMENTAL.....	15
CONCLUSIONS.....	24
APPENDIX.....	25
REFERENCES.....	39

DEVELOPMENT OF SILOXANE-CONTAINING EPOXY POLYMERS
FOR ELECTRICAL CIRCUIT EMBEDMENT APPLICATIONS

SUMMARY

A synthesis and development program is being directed toward high performance embedment of encapsulating compounds for use in cordwood module circuitry on launch vehicles. This report describes the development of seven siloxane-containing epoxy resin precursors and subsequent polymerization of these precursors into thermosetting, useful embedment compounds. The incorporation of successively longer polysiloxane moieties within these epoxy intermediates was found to improve dielectric properties of the resulting polymers. Various structural modifications were represented by this series of epoxides in order to obtain the optimum balance of flexibility and electrical properties required in the embedment application.

Several siloxane-containing diamines were prepared as polymerization agents for the epoxides. These amines demonstrated, by virtue of the siloxane groups, increased compatibility with the siloxane-epoxides so that homogeneous solutions of the amine in the epoxide were formed under conditions where the use of conventional organic, aromatic amines resulted in heterogeneous mixtures.

Dielectric property data were obtained from polymers resulting from ten formulations of the epoxides. The best dielectric properties were obtained from a polymer formed from 1,9-bis(p-(2,3-epoxypropyl)phenyl)-decamethylpentasiloxane (XX), which had a dielectric constant and dissipation factor of 3.1 and 0.01, respectively. This polymer was very flexible at 25°C and stiff but non-brittle at -75°C. However, the tensile strength and toughness of these polymers appeared to decrease as a function of increasing siloxane content. The polymer formed from 1,4-bis((p-(2,3-epoxypropyl)phenyldimethylsiloxy)dimehtylsilyl)benzene (XXII) was considered to have the optimum combination of toughness, flexibility and dielectric properties for the embedment application.

INTRODUCTION

The development of improved polymeric materials for the embedment of electronic circuitry of the cordwood module type has been the basis of a continuing program. This report describes the synthesis and

polymerization of a series of siloxane-containing epoxy intermediates, and evaluation of the polymers derived from them. The scope of the synthetic approach has been to prepare di- or trifunctional polymer precursors which polymerize with diamines into crosslinked thermosetting products. The alternative procedure would involve a partial polymerization of the difunctional monomer to a liquid prepolymer which would then be crosslinked to a solid resin. This introduces inherent problems of controlling the degree of polymerization of the prepolymer to reproducibly obtain the required epoxide functionality. Purification of the prepolymer is also much more difficult than in the precursor form. Thus, in the interest of producing polymers whose structures were predictable in terms of functionality, which appeared desirable to minimize dielectric breakdown, outgassing, and structural failure, the concept of the polymer precursor has been utilized.

The historical development of polymerizable siloxane-containing epoxides has recently been reviewed by Bilow, et. al. (ref. 1) in some detail. The work cited by this reference concerned the investigation of polyfunctional epoxides containing the siloxane linkage in various structural forms. Thus, polymerizable epoxides containing the disiloxane linkage have been reported as characterizable compounds, and the preparation of various structural homologs of these compounds has been attempted via cohydrolysis reactions involving the ethoxy-silane group.

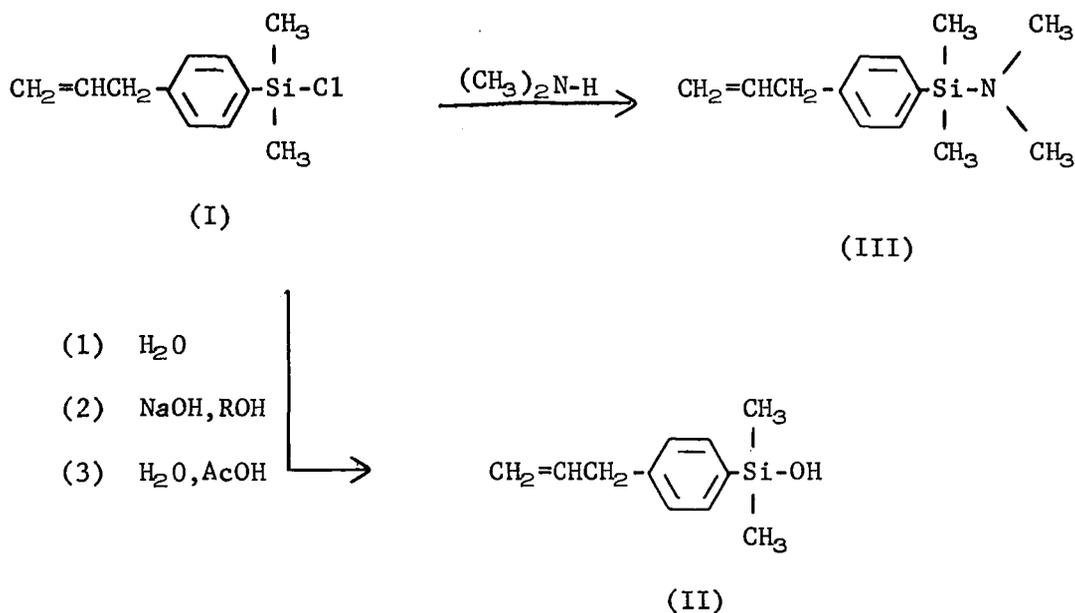
The disiloxane linkage appears to contribute to dielectrically attractive properties when incorporated in crosslinked epoxy polymers. It became of interest to assess the effect of increasing the siloxane chain length in both linear and branched structures on the electrical properties of the resulting polymers, and to determine qualitatively the physical and mechanical properties of these polymers.

Thus, the current study concerns the preparation of seven analytically characterizable epoxides via the facile silanol-aminosilane condensation. These polymer precursors were subsequently polymerized with amines into stable, thermosetting materials. Dielectric property data have been obtained for the polymers in an effort to determine the effects of structural variations on these properties.

DISCUSSION

Formation of Polymer Intermediates

The reaction schemes followed to prepare five of the seven desired epoxides utilized p-allylphenyldimethylchlorosilane (I) as a common starting compound.

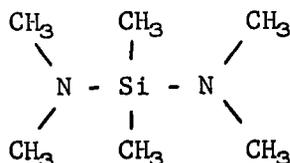


(I) was prepared by the method of Bilow, et.al. (ref. 1) by condensation of the grignard reagent of *p*-allylbromobenzene with dimethyldichlorosilane. Compound (I) was hydrolyzed through a multistep procedure involving the sodium silanolate to yield *p*-allylphenyldimethylsilanol (II). Attempts to convert (I) to (II) by a one-step basic hydrolysis with sodium hydroxide were unsuccessful, resulting invariably in the formation of the dimer, 1,3-bis(*p*-allylphenyl)tetramethyldisiloxane. This was somewhat surprising in view of the facile conversion of 1,4-bis(chlorodimethylsilyl)benzene to the corresponding disilanol, 1,4-bis(hydroxydimethylsilyl)benzene (X) which was prepared by the one-step method (ref. 2). Apparently the intermediate (II) more readily forms the silanolate ion through the influence of the *p*-allyl group. Compound (II) was successfully prepared by formation of the sodium salt and subsequent acid hydrolysis after the method of Hyde (ref. 3). This compound can be distilled in the absence of acid or base to yield an analytically pure sample.

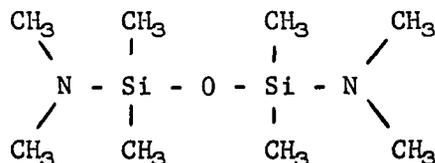
The infrared spectrum of (II) is shown in figure 1. The intense silanol hydroxyl stretch is noted at 3300 cm^{-1} . The strong peaks at 1260 cm^{-1} and 1120 cm^{-1} , are generally attributed to silicon-methyl and silicon-phenyl vibrations, respectively.

p-Allylphenyldimethylaminodimethylsilane (III) was prepared by direct treatment of (I) with anhydrous dimethylamine in the cold. The aminosilanes prepared in this study were highly moisture sensitive, due to the ease of hydrolysis of the Si-N bond and the tendency to form the more stable siloxane bond. Faint white precipitates tend to form in the aminosilanes unless a very dry atmosphere is maintained.

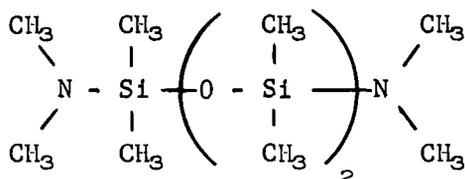
The six remaining aminosilanes, bis(dimethylamino)dimethylsilane (IV), 1,3-bis(dimethylamino)tetramethyldisiloxane (V), 1,5-bis(dimethylamino)hexamethyltrisiloxane (VI), tris(dimethylamino)methylsilane (VII), vinyl dimethylaminodimethylsilane (VIII), and dimethylaminodimethylsilane (IX) were prepared by aminolysis of the corresponding chlorides following the method for compound (III).



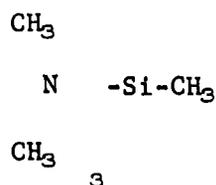
(IV)



(V)

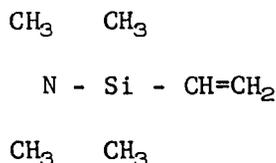


(VI)

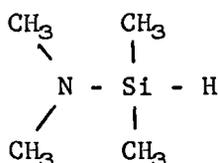


3

(VII)



(VIII)



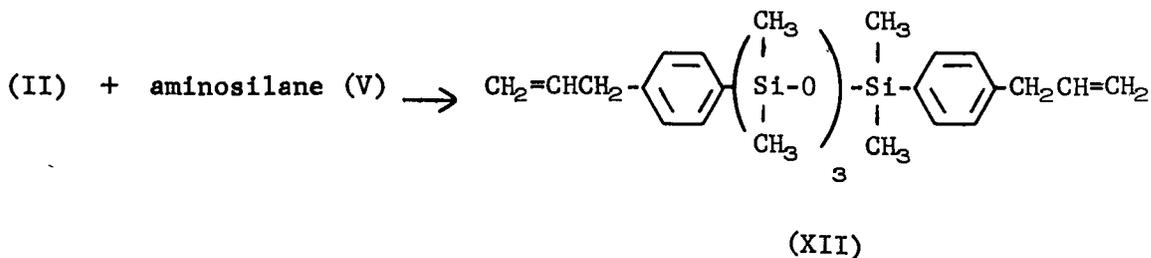
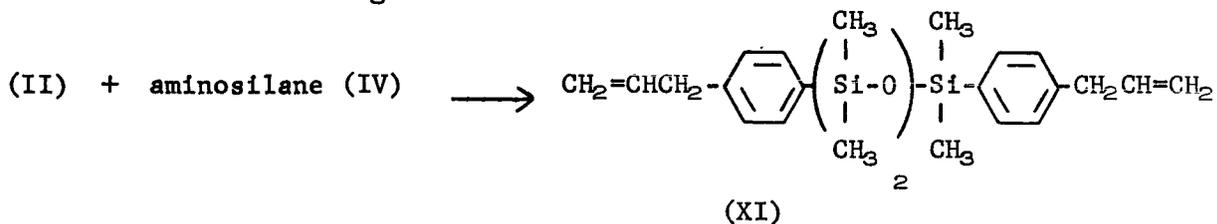
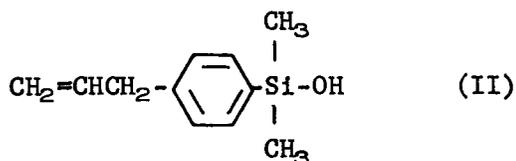
(IX)

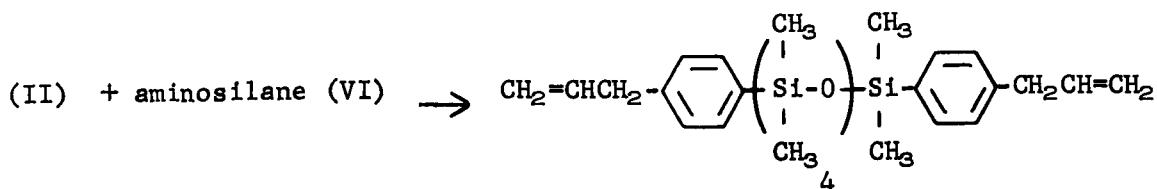
The $(\text{CH}_3)_2\text{N-Si}$ structure in compounds (III-IX) is characterized by intense infrared absorption at $980-1000 \text{ cm}^{-1}$, as indicated in figures 2-8. The characteristic broad Si-O-Si absorption, which is unique within this series to compounds (V) and (VI), is observed at $1070-1100 \text{ cm}^{-1}$ in figures 4 and 5. The characteristic Si-H absorption exhibited by compound (IX) is observed at 2140 cm^{-1} in figure 8.

Aminosilane-Silanol Condensations

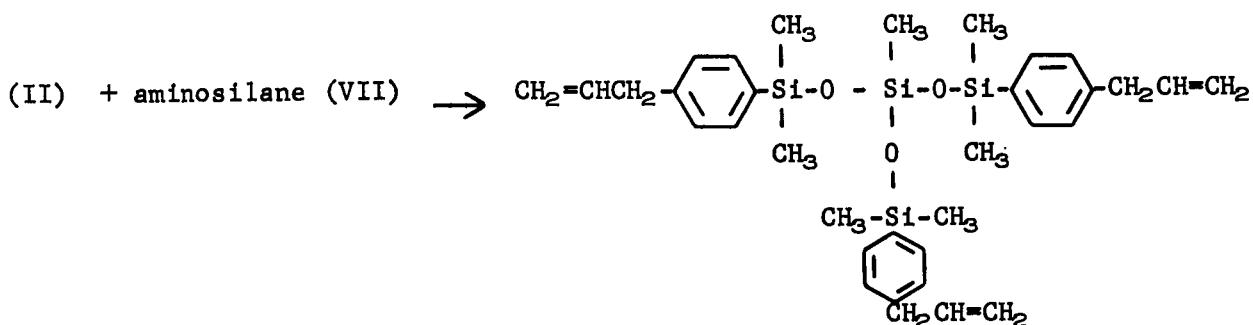
The dimethylaminosilane derivatives were preferred for this condensation reaction over the corresponding monomethylaminosilanes due to their relative stability. The monomethyl compounds have a higher tendency to homopolymerize with evolution of methylamine. Also, according to Pike (ref. 4), the dialkylaminosilanes condense at a faster rate with silanols than do the monoalkylaminosilanes. Apparently the increased basicity of the dialkylaminosilanes more than compensates for the additional steric hindrance introduced by the second methyl group. Thus, the facile condensation of aminosilane with silanol has been utilized to prepare the compounds 1,5-bis(*p*-allylphenyl)hexamethyltrisiloxane (XI), 1,7-bis(*p*-allylphenyl)octamethyltetrasiloxane (XII), 1,9-bis(*p*-allylphenyl)decamethylpentasiloxane (XIII), tris(*p*-allylphenyldimethylsiloxy)methylsilane (XIV), 1,4-bis((*p*-allylphenyldimethylsiloxy)dimethylsilyl)benzene (XV), 1,4-bis((vinyl dimethylsiloxy)dimethylsilyl)benzene (XVI), and 1,4-bis(dimethylsiloxy)dimethylsilyl)benzene (XVII).

Compounds (XI), (XII), (XIII), and (XIV) were prepared directly from silanol (II) and the appropriate aminosilane, as indicated in the reaction sequences below:



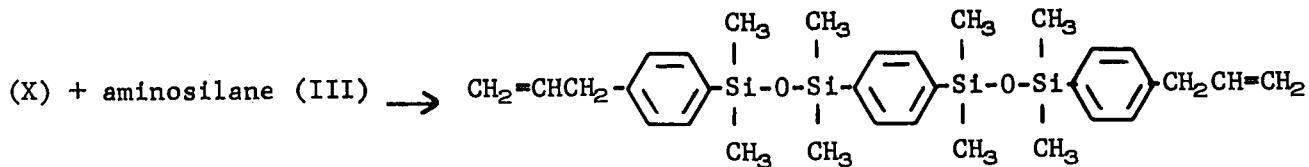
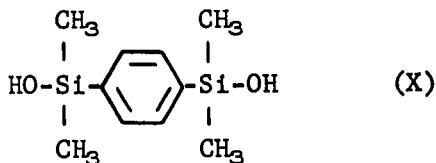


(XIII)

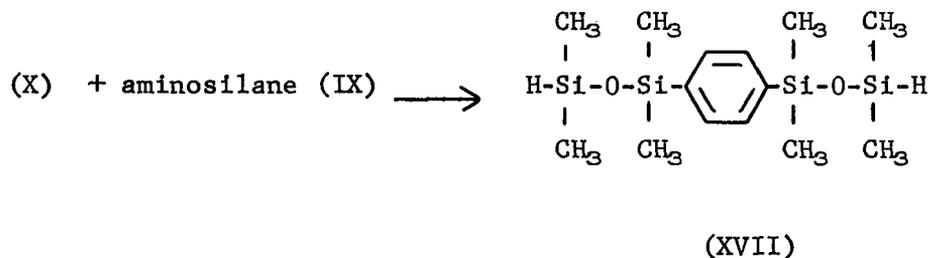
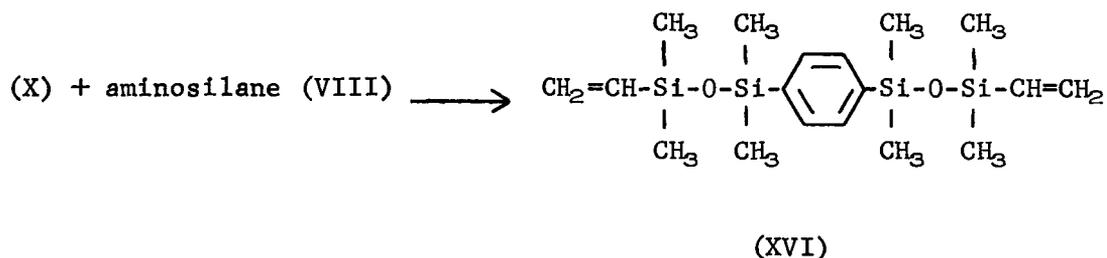


(XIV)

The remaining intermediates (XV), (XVI), and (XVII), were prepared with 1,4-bis(hydroxydimethylsilyl)benzene (X) as a common precursor:



(XV)



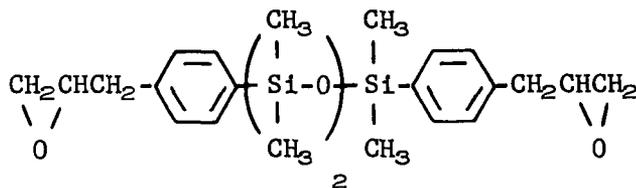
The complete disappearance of the silanol and silicon-nitrogen infrared absorptions at 3300 cm^{-1} and 990 cm^{-1} , respectively, and subsequent predominance of the intense open chain Si-O-Si vibration at $1050\text{-}1100\text{ cm}^{-1}$ is observed in figures 10-16. Compound (XVII), which is the only one of the above series not terminating in an olefinic group, retains the reactive silicon hydride group following the silanol-aminosilane condensation as evidenced by the intense absorption at 2140 cm^{-1} in figure 16.

The addition sequence utilized in formation of compounds (XI) through (XIV) affected the yields to a small extent. The conventional sequence would involve addition of the appropriate polyfunctional aminosilanes to the monofunctional diol (II). To assess the extent of undesirable silanol dehydration in the conventional addition sequence, compound (II) was refluxed in methylene chloride with and without the addition of catalytic amounts of aminosilane (IV). An amount of water equivalent to approximately 10 percent dehydration was recovered in a Dean-Stark trap from the aminosilane-catalyzed silanol solution, whereas no water was recovered from the silanol solution which had not been treated with aminosilane. This observation was also borne out in the yields of compounds (XI) through (XIV), which were 5 to 10 percent higher for the addition sequence of silanol to aminosilane. This sequence was utilized as the normal procedure for preparation of compounds (XV) through (XVII). In these cases, the silanol, 1,4-bis(hydroxydimethylsilyl)benzene (X), served as the difunctional monomer and the aminosilane was monofunctional.

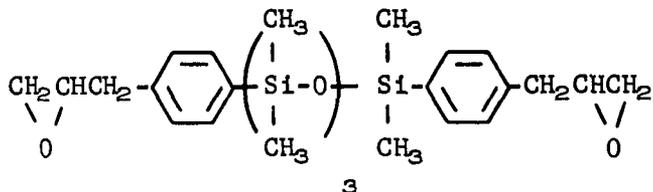
Previous preparative studies (ref. 1) of compounds (XI), (XIV), and (XV) involved cohydrolysis reactions of the ethoxy-silane group which resulted in formation of the desired structures plus other condensation products having both lower and higher degrees of polymerization of the siloxane moiety. In the present work, condensations of silanol and aminosilane were effected in the melt or in a solvent, with low boiling dimethylamine as the only major by product. The course of these condensations was followed by neutralization of the evolved amine with standard acid, and in each case the condensations appeared to proceed to within 90-95 percent of the theoretical value.

Epoxidations

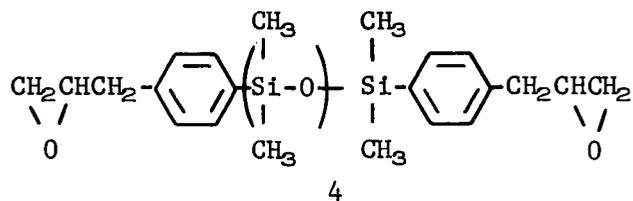
The series of epoxides prepared from compounds (XI) through (XVII) reflects the various procedures investigated in order to efficiently incorporate the oxirane ring in terminal positions on these compounds. Compounds (XI) through (XVI) were converted to the corresponding epoxides, 1,5-bis(*p*-(2,3-epoxypropyl)phenyl)hexamethyltrisiloxane (XVIII), 1,7-bis(*p*-(2,3-epoxypropyl)phenyl)octamethyltetrasiloxane (XIX), 1,9-bis(*p*-(2,3-epoxypropyl)phenyl)decamethylpentasiloxane (XX), methyltris(*p*-(2,3-epoxypropyl)phenyldimethylsiloxy)silane (XXI), 1,4-bis((*p*-(2,3-epoxypropyl)phenyldimethylsiloxy)dimethylsilyl)benzene (XXII), and 1,4-bis((epoxyethyl)dimethylsiloxy)dimethylsilyl)benzene (XXIII), respectively, by modifications of the trifluoroacetic acid epoxidizing technique (ref. 5):



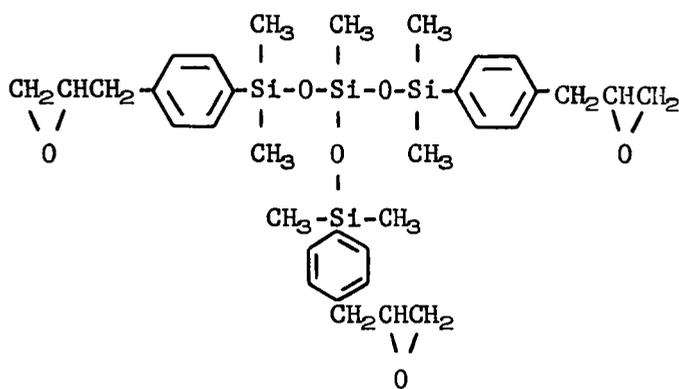
(XVIII)



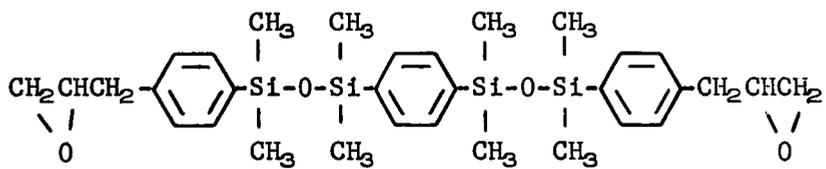
(XIX)



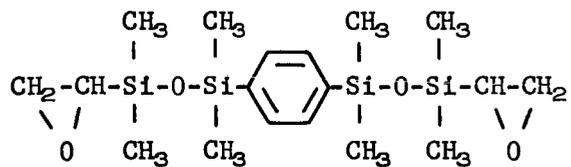
(XX)



(XXI)

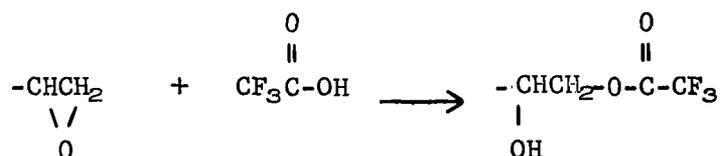


(XXII)



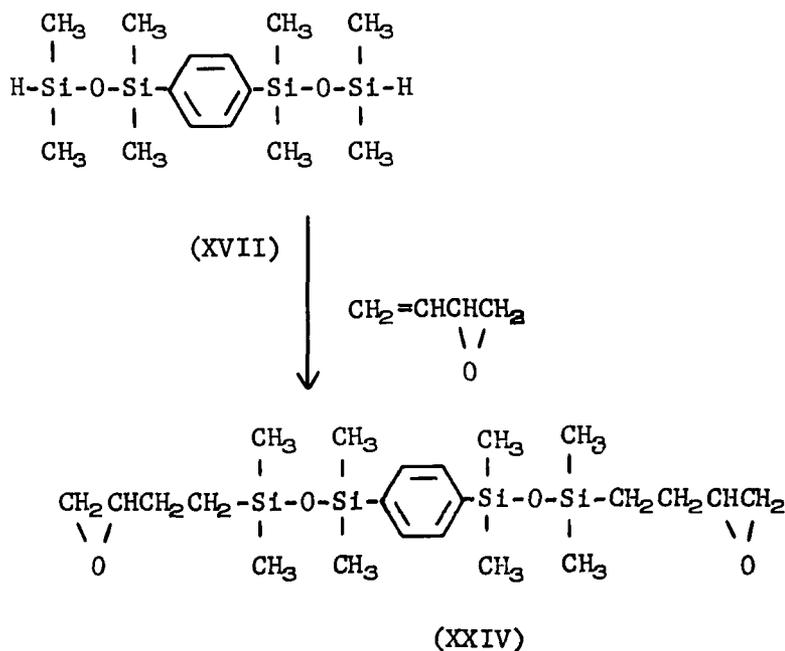
(XXIII)

Epoxidation of the terminal double bonds in these compounds proceeded quite readily with the peracid. It is of interest to note that the optimum reaction temperature to form (XVIII) through (XXII) was 30-40°C with only a moderate excess of sodium carbonate as scavenger for the liberated trifluoroacetic acid, whereas (XXIII) formed efficiently at 0-5°C in the presence of a large excess of potassium carbonate. These temperatures represent the conditions under which the respective epoxides are formed with a minimum of trifluoroacetate contamination, which can form in the following fashion:



Although reaction rate studies for esterification within the two epoxidation procedures have not been performed, it is evident that the epoxides prepared from the allyl derivatives suffer gross esterification at temperatures where the epoxide prepared from the vinyl derivative survives virtually intact. The low temperature epoxidation conditions are somewhat more flexible than those for the higher temperature procedure, since there is no critical carbonate concentration. The yields of uncontaminated epoxide are higher in the low temperature procedure.

The preparation of the seventh epoxide of the series, 1,4-bis((3,4-epoxybutyldimethylsiloxy)dimethylsilyl)benzene (XXIV), involved the addition reaction of a silicon hydride with a terminal double bond:



This reaction proceeded smoothly with a noticeable exotherm in the presence of chloroplatinic acid catalyst at 70-75°C. During attempts to optimize the conditions for this reaction, an apparent threshold reaction temperature was observed at 60-70°C. The entire addition of silicon hydride to olefin could be carried out below 60°C without observing evidence of reaction. Then, as the temperature was increased to 70-75°C, the reaction mixture containing the entire charge of silicon hydride became violently exothermic and resulted in discoloration of the products.

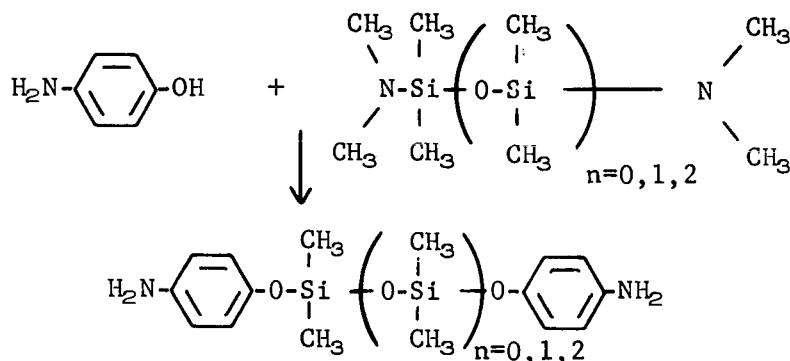
The extent of reaction occurring after the dropwise addition of the silicon hydride at 70-75°C was determined by the disappearance of the Si-H absorption peak at 2100-2200 cm⁻¹. This peak normally disappeared within one-half hour after the addition was complete. The addition product, compound (XXIV), was obtained in crude form in 85-90 percent yield.

The infrared spectra of compounds (XVII) through (XXII) indicated the presence of the epoxy ring by weak absorptions at 930-960 cm⁻¹ and 740-760 cm⁻¹ in figures 17 through 21. Compound (XXIII), having the epoxy group adjacent to a silicon atom, was characterized by a moderate infrared absorption at 890 cm⁻¹ and a weaker absorption at 1325 cm⁻¹ in figure 22. These bonds become apparent on comparison of epoxide (XXIII) with its divinyl precursor (XVI) in figure 15. A probable assignment for the epoxy group in compound (XXIV) is the weak absorption at 910 cm⁻¹.

Infrared assignments for epoxy-containing organosilicon compounds must, in general, be made on the strength of the moderate or weak bands, because the characteristic epoxy bands at 1250-1260 cm⁻¹ are often obscured by the more intense silicon-alkyl absorptions.

Curing Agents

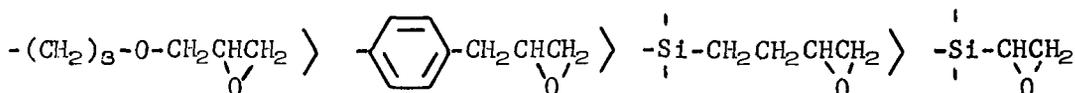
A series of amine curing agents was prepared specifically for investigation as curing agents when it was observed that more common amines were incompatible with the siloxane-containing epoxide prepolymers. Diamines containing siloxane linkages were prepared by way of an amino-silane-phenol condensation:



The aminosilanes (IV), (V), and (VI), discussed previously under the section on polymer intermediates, were utilized directly in the condensation with *p*-aminophenol. The phenol was sublimed prior to the reaction. Three siloxane-amines, bis(*p*-aminophenoxy)dimethylsilane (XXV), (ref. 6), 1,3-bis(*p*-aminophenoxy)tetramethyldisiloxane (XXVI) and 1,5-bis(*p*-aminophenoxy)-hexamethyltrisiloxane (XXVII), were prepared by this method for polymerization with the siloxane-epoxides described in the previous section. The liquid state of (XXVI) and (XXVII) in addition to siloxane content greatly facilitated their formulation with the siloxane-epoxides. The increased solubility of these siloxane-amines in the epoxides was demonstrated by the fact that *m*-phenylenediamine was completely insoluble in compound (XXIV) at 100°C whereas compound (XXVI) formed a true solution with (XXIV) at room temperature. An additional advantage to be gained in utilizing the siloxane-modified amines lies in the dielectric properties of polymers prepared with these compounds. The increased siloxane concentration along the polymer chain served to reduce the overall polarity of the polymer, resulting in lower dielectric losses.

Polymerizations

Epoxides (XVIII) through (XXIV), except (XXIII), were each polymerized with freshly prepared siloxane-diamines at 100°C until solid, thermosetting polymers were formed. One mole-equivalent of diepoxide was polymerized with 0.95 mole-equivalent of diamine, with the exception of the trifunctional epoxide (XXI), in which case one mole-equivalent of epoxide was polymerized with 1.42 mole-equivalents of diamine. The polymerization conditions for the various epoxides are summarized in Table I. The epoxides (XVIII) through (XXII) polymerized quite readily at 100°C with the disiloxane diamine (XXVI) to form tough thermosetting materials. The flexibility of these polymers was, in general, proportional to the length of the siloxane moieties present in the polymer backbone, as evidenced in Table I, formulations 1-3. The trifunctionality of compound (XXI) contributed to a significantly higher crosslink density and greater toughness in the cured polymer (formulation 4). The reactivity of the epoxy group in compounds (XXIII) and (XXIV) toward the aromatic amine was significantly lower than in the compounds just discussed. Compound (XXIV) polymerized sluggishly at 100°C and (XXIII) would not polymerize to a thermosetting solid at this temperature without substituting a more reactive aliphatic amine. For comparative purposes a commercial diepoxide (Diglycidyl ether of bisphenol-A, Epon X-24, Shell Chemical Company) was polymerized under these conditions to yield a solid product after four hours. Thus, a general reactivity sequence is indicated for polymerization with aromatic amine at 100°C:



This suggests that the silicon atom decreases the susceptibility of the primary carbon atom to nucleophilic attack by the amine.

TABLE I.- Polymerization Conditions for Epoxy-Siloxane Intermediates

Formulation	Epoxyde	Amine	Epoxyde/Amine		Polymerization ***		Polymer Appearance
			Molar Ratio	Molar Ratio	Time (Hours)	Time (Hours)	
1	XVIII	XXVI	1.0/0.95	1.0/0.95	24	24	Semi-flexible, tough amber solid
2	XIX	XXVI	1.0/0.95	1.0/0.95	24	24	Flexible, tough amber solid
3	XX	XXVI	1.0/0.95	1.0/0.95	24	24	Very flexible amber solid
4	XXI	XXVI	1.0/1.42	1.0/1.42	24	24	Glassy, amber solid
5	XXII	XXVI	1.0/0.95	1.0/0.95	24	24	Semi-flexible, very tough amber solid
6	XXIII	EDA*	1.0/0.95	1.0/0.95	24	24	Glassy, dark solid
7	XXIV	XXVI	1.0/0.95	1.0/0.95	48	48	Glassy, amber solid
8	XVIII + XXI	XXVI	0.9, 0.1/0.99	0.9, 0.1/0.99	24	24	Semi-flexible, very tough solid
9	XVII	XXV	1.0/0.95	1.0/0.95	24	24	Semi-flexible, tough solid
10	XVIII	XXVII	1.0/0.95	1.0/0.95	24	24	Flexible, tough solid
11	**	XXVI	1.0/0.95	1.0/0.95	24	24	Semi-flexible, tough solid

* EDA: Ethylenediamine

** 1,3-Bis(p-(2,3-epoxypropyl)phenyl)tetramethyldisiloxane

*** Polymerization Temperature: 100°C.

Formulations 1 through 11 were polymerized in the form of castings from which two-inch diameter, 1/16-inch thick dielectric test specimens were fabricated. The dielectric measurements were performed at 25°C and a frequency of one kilocycle. These results are given in Table II:

TABLE II.- Dielectric Data for Epoxy-Siloxane Polymers

<u>Formulation</u>	<u>Dielectric Constant</u>	<u>Dissipation Factor</u>
1	3.2	0.03
2	3.2	0.025
3	3.1	0.010
4	3.4	0.025
5	3.2	0.02
6	4.5	0.05
7	3.8	0.03
8	3.4	0.025
9	3.5	0.02
10	3.2	0.04
11*	3.3	0.01

* Polymer formed from 1,3-bis(p(2,3-epoxypropyl)phenyl)tetramethyldisiloxane (ref. 1) and compound (XXVI).

Comparative data have been presented for the polymer formed from the disiloxane homolog of this series (ref. 1). All polymer specimens for which the data in Table II were obtained were polymerized, fabricated, and tested under carefully controlled conditions so that subtle differences in dielectric values between formulations would be more meaningful.

EXPERIMENTAL

The starting silane compounds were obtained from Peninsular ChemResearch, Gainesville, Florida, and were redistilled prior to use. The infrared spectra from smears of the products were recorded in the 2.5-15.0 μ region with a Perkin-Elmer model 137 double beam spectrophotometer equipped with sodium chloride optics. Molecular weights were determined in benzene with a 37°C. probe with a Mechrolab model 302 vapor pressure osmometer. Molecular distillations were performed with a Nester-Faust semi-micro molecular still. The epoxide equivalent weights were determined by titration with hydrogen bromide in acetic acid.

Preparation of *p*-Allyldimethylchlorosilane (I)

Compound (I) was prepared by the condensation of dimethyldichlorosilane with the Grignard reagent of *p*-allylbromobenzene, after the method of Bilow, et.al. (ref. 1). The pale yellow oil was recovered in 40 percent yield, boiling point 70-71°C/0.8 torr, literature boiling point 102-103°C/5 torr, (ref. 1). Routine elemental analyses were unsatisfactory for compound (I) because of its sensitivity to moisture. End group determination of ionizable chloride was performed.

Analyses Calculated for C₉H₁₅ClSi: Si, 16.8%. Found: Si, 16.84%.

Preparation of *p*-Allylphenyldimethylsilanol (II)

Initial attempts to prepare (II) by direct hydrolysis with a mixture of water, ammonium hydroxide, and ether under various conditions were unsuccessful and resulted in predominant formation of the dimer, 1,3-bis(*p*-allylphenyl)tetramethyldisiloxane. Compound (II) was successfully prepared by first adding 10 grams (0.0476 mole) of (I) with rapid stirring to a mixture consisting of a ten-mole excess of 10 percent aqueous sodium bicarbonate and 280 ml. of ether. The dimer, 1,3-bis(*p*-allylphenyl)tetramethyldisiloxane, was recovered in 95 percent yield in crude form. The product was distilled at 135-140°C/0.02 torr, literature boiling point 130-140°C/0.01 torr (ref. 1). The dimer, 10 grams, 0.0273 mole, was added dropwise to a stirred solution of 2.2 grams, 0.055 mole of sodium hydroxide in 20.8 ml. anhydrous methanol and 48.5 ml. anhydrous isopropanol at 40-50°C according to the procedure of Hyde (ref. 3). Following the addition, the mixture was heated to 115°C and concentrated to a thick slurry. The precipitating solid was redissolved in methanol with heating and evacuated on a water aspirator at 140°C. This was repeated twice more. The sodium *p*-allylphenyldimethylsilanolate thus prepared was slurried with ether and added slowly to a

stirred mixture of 8.1 ml. acetic acid, 104 ml. ether, and 208 ml. water which was maintained at 0-5°C. The ether phase was recovered, washed to neutrality with cold H₂O, and dried over anhydrous magnesium sulfate. The residue was distilled at 83-85°C/0.15 torr in 85 percent yield.

Analyses Calculated for C₁₁H₁₆OSi: C, 68.7%; H, 8.3%; Si, 14.6%.
Found: C, 68.59%; H, 9.18%; Si, 15.12%.

Molecular Weight Calculated: 192. Found: 212 (determined in benzene by vapor pressure osmometry).

Preparation of p-Allylphenyldimethylaminodimethylsilane (III)

Compound (I), 10 grams, 0.0476 mole, was added dropwise to a stirred solution of excess anhydrous dimethylamine in ether which was maintained at 0°C. The mixture was stirred for one hour following the addition, during which time the reaction temperature was allowed to return to 25°C. The mixture was filtered to remove the amine hydrochloride, and compound (III) was recovered in 89 percent yield as a colorless oil, boiling point 82-85°C/0.25 torr.

Analyses Calculated for C₁₃H₂₁NSi: Si, 12.8%; N, 6.38%.
Found: Si, 12.63%; N, 6.0%.

Preparation of Bis(dimethylamino)dimethylsilane (IV)

Freshly distilled dimethyldichlorosilane, 50 grams, 0.39 mole, was added dropwise to a stirred solution of excess anhydrous dimethylamine in ether which was maintained at 0°C. Reaction conditions and workup were similar to those described for compound (III). The crude reaction product was distilled at 118°C/760 torr and represented a 75 percent yield.

Analyses Calculated for C₆H₁₈N₂Si: N, 19.18%; Si, 19.18%.
Found: N, 18.28%; Si, 19.45%.

Preparation of 1,3-Bis(dimethylamino)tetramethyldisiloxane (V) and 1,5-Bis(dimethylamino)hexamethyltrisiloxane (VI)

The preparation of (V) and (VI) necessitated the preparation of the respective chlorides. 1,3-Dichlorotetramethyldisiloxane and 1,5-dichlorohexamethyltrisiloxane were prepared by the method of Breed et al. The disiloxane was recovered in 25 percent yield, boiling point 136-138°C/760 torr, literature boiling point 41°C/20 torr (ref. 7), whereas a 15 percent yield of trisiloxane was recovered, boiling point 79°C/20 torr, (ref. 7). 1,3-Dichlorotetramethyldisiloxane, 50 grams, 0.24 mole, and 1,5-dichlorohexamethyltrisiloxane, 50 grams, 0.18 mole, were added in separate operations to excess dimethylamine, following the amination procedure described earlier. The

1,3-bis(dimethylamino)tetramethyldisiloxane was recovered in 80 percent yield as a colorless oil, boiling point 55-57°C/5 torr; the 1,5-bis-(dimethylamino)hexamethyltrisiloxane was recovered in 85 percent yield as a colorless oil, boiling point 105-106°C/2 torr.

Analyses Calculated for $C_8H_{24}N_2OSi_2$: Si, 24.45%; N, 12.73%.
Found: Si, 24.95%; N, 11.73%.

Calculated for $C_{10}H_{30}N_2O_2Si_3$: Si, 28.57%; N, 9.52%. Found: Si, 28.52%; N, 8.72%.

Preparation of Methyl-tris(dimethylamino)silane (VII)

Freshly distilled methyltrichlorosilane, 50 grams, 0.338 mole, was added dropwise to a stirred solution of excess anhydrous dimethylamine in ether, following the previously described amination procedures. The product was recovered in 82 percent yield as a colorless oil, boiling point 152-153°C/760 torr.

Analyses Calculated for $C_7H_{21}N_3Si$: N, 24.0%; Si, 16.0%.
Found: N, 23.96%; Si, 16.55%.

Preparation of Vinyl dimethylaminodimethylsilane (VIII)

Freshly distilled vinyl dimethylchlorosilane, 50 grams, 0.416 mole) was added to an excess of anhydrous dimethylamine following the previously described amination procedures. The product was recovered by fractional distillation in 73 percent yield as a colorless oil, boiling point 105-106°C/760 torr.

Analyses Calculated for $C_6H_{15}NSi$: N, 10.85%; Si, 21.7%.
Found: N, 11.22%; Si, 21.9%.

Preparation of Dimethylaminodimethylsilane (IX)

Dimethylchlorosilane, 103 grams, 1.0 moles, was added dropwise to excess anhydrous dimethylamine in ether following previously described amination procedures. Compound (IX) was recovered by fractional distillation in 86 percent yield, boiling point 65-66°C/760 torr.

Analyses Calculated for $C_4H_{13}NSi$: N, 11.88%; Si, 27.72%.
Found: N, 10.92%; Si, 27.55%.

Preparation of 1,4-Bis(hydroxydimethylsilyl)benzene (X)

Compound (X) was prepared according to the method of Sveda (ref. 2) in 75 percent yield as white crystals, melting point 135-136°C, literature melting point 135°C (ref. 2).

Analyses Calculated for $C_{10}H_{18}O_2Si_2$: C, 53.09%; H, 7.96%; Si, 24.80%. Found: C, 52.3%; H, 8.24%; Si, 24.78%.

Preparation of 1,5-Bis(p-allylphenyl)hexamethyltrisiloxane (XI)

To bis(dimethylamino)dimethylsilane (IV), 5.07 grams, 0.0347 mole, was added dropwise p-allylphenyldimethylsilanol (II), 20 grams, 0.104 mole, which was stirred under nitrogen at room temperature. The nitrogen purge stream was bubbled into a known volume and normality of aqueous HCl. No exotherm was detected at 25°C and the reaction temperature was slowly increased to 50°C, where dimethylamine began to evolve. The reaction temperature was held for one hour at 50°C, 75°C, and 100°C, successively. The pressure was reduced to 30-35 torr during the last hour. Calculation of the amine evolved, by back titration of the acid solution with standard base, indicated that the condensation was 95.5 percent complete. The crude liquid condensation product was neutral to wet pH paper and had a light straw color. Distillation in a molecular still resulted in a pale yellow oil in 85 percent yield, boiling point 146-151°C/10⁻³ torr.

Analyses Calculated for $C_{24}H_{36}O_2Si_3$: C, 65.45%; H, 8.18%; Si, 19.09%. Found: C, 66.79%; H, 8.70%; Si, 19.25%.

Calculated Molecular Weight: 440. Found (VPO): 429

Preparation of 1,7-Bis(p-allylphenyl)octamethyltetrasiloxane (XII)

To 1,3-bis(dimethylamino)tetramethyldisiloxane (V), 5 grams, 0.023 mole, was added p-allylphenyldimethylsilanol (II), 8.83 grams, 0.047 mole, using the procedure described for compound (VIII). The crude yield was 94 percent, determined by amine titration. The product was recovered in 84 percent yield by molecular distillation, boiling point 168°C/10⁻³ torr.

Analyses Calculated for $C_{26}H_{42}O_3Si_4$: C, 60.70%; H, 8.17%; Si, 21.79%. Found: C, 61.35%; H, 8.50%; Si, 21.43%.

Preparation of 1,9-Bis(p-allylphenyl)decamethylpentasiloxane (XIII)

To 1,5-bis(dimethylamino)hexamethyltrisiloxane, (VI), 5 grams, 0.017 mole, was added p-allylphenyldimethylsilanol (II), 6.53 grams, 0.035 mole, using the procedure outlined for compound (VIII). The crude yield was 95 percent, determined by amine titration. The product was recovered by molecular distillation in 82 percent yield as a pale yellow oil, boiling point 174-179°C/10⁻³ torr.

Analyses Calculated for $C_{28}H_{48}O_4Si_5$: C, 57.14%; H, 8.16%; Si, 23.81%. Found: C, 56.82%; H, 8.05%; Si, 23.65%.

Preparation of Methyl-tris(p-allylphenyldimethylsiloxy)silane (XIV)

To methyl-tris(dimethylamino)silane (VII), 6.05 grams, 0.0346 mole, was added p-allylphenyldimethylsilanol (II), 20 grams, 0.104 mole, following the procedures described previously. A crude yield of 93 percent was obtained as indicated by amine titration. Compound (XIV) was recovered in 80 percent yield by molecular distillation, boiling point 165-170°C/10⁻⁴ torr.

Analyses Calculated for C₃₄H₄₈O₃Si₄: C, 66.23%; H, 7.79%; Si, 18.18%. Found: C, 65.82%; H, 6.93%; Si, 19.35%.

Calculated Molecular Weight: 616. Found (VPO): 602.

Preparation of 1,4-Bis((p-allylphenyldimethylsiloxy)dimethylsilyl)benzene (XV)

1,4-Bis(hydroxydimethylsilyl)benzene (X), 10.3 grams, 0.045 mole, was recrystallized to a constant melting point from toluene/petroleum ether and added as an ether solution to p-allylphenyldimethylamino-dimethylsilane (III), 20 grams, 0.0913 mole, at 25°C. A continuous evolution of amine was observed throughout the addition. The mixture was subsequently heated to 50°C for 1/2-hour to remove ether and at 75°C for 1/2-hour under aspirator vacuum. A 96 percent yield of crude compound (XV) was recovered as indicated by amine titration. Molecular distillation of the crude product produced an 83 percent yield of light yellow oil, boiling point 154-159°C/5×10⁻⁴ torr.

Analyses Calculated for C₃₂H₄₆O₂Si₄: C, 66.90%; H, 8.01%; Si, 19.51%. Found: C, 65.95%; H, 7.85%; Si, 19.62%.

Calculated Molecular Weight: 574. Found: 565.

Preparation of 1,4-Bis((vinyl)dimethylsiloxy)dimethylsilyl)benzene (XVI)

1,4-Bis(hydroxydimethylsilyl)benzene (X), 17.5 grams, 0.0775 mole, was added to vinyldimethylaminodimethylsilane (VIII), 20 grams, 0.155 mole, following the procedures previously described for compound (XV). Fractional distillation of the crude product resulted in an 81 percent yield of colorless oil, boiling point 110-113°C/0.1 torr.

Analyses Calculated for C₁₈H₃₄O₂Si₄: C, 54.82%; H, 8.63%; Si, 28.42%. Found: C, 54.21%; H, 9.40%; Si, 28.88%.

Calculated Molecular Weight: 394. Found: 388.

Preparation of 1,4-Bis(dimethylsiloxy)dimethylsilyl)benzene (XVII)

1,4-Bis(hydroxydimethylsilyl)benzene (X), 10 grams, 0.044 mole, was added to dimethylaminodimethylsilane (IX), 8.9 grams, 0.089 mole, following the procedures outlined for compound (XV). The crude product was recovered in 92 percent yield by fractional distillation, boiling point 95-96°C/5 torr.

Analyses Calculated for $C_{14}H_{30}O_2Si_4$: C, 49.12%; H, 8.77%; Si, 32.75%. Found: C, 48.50%; H, 8.95%; Si, 31.9%.

Calculated Molecular Weight: 342. Found (VPO): 350.

The epoxidation procedures utilized to prepare compounds (XVIII) through (XXIII) consisted of a slight modification of the procedure of Eisch et.al. (ref. 5). Oxirane equivalents for compounds (XVIII) through (XXIV) were determined by the hydrobromic acid method. The concentrated hydrogen peroxide (Shell Chemical Company) was determined to be 89.5 percent active by the permanganate method. The carbonate acid-scavengers were ground for several hours in a ball mill and dried over phosphorus pentoxide at 100°C/5 torr overnight.

Preparation of 1,5-Bis(p-(2,3-epoxypropyl)phenyl)hexamethyltrisiloxane (XVIII)

A mixture of 89.5 percent hydrogen peroxide, 1.74 grams, 0.0456 mole, and 25 ml. of methylene chloride was cooled to 0-5°C. To this stirred mixture was added trifluoroacetic anhydride, 11.8 grams, 0.0562 mole, dropwise, while maintaining the temperature at 0-5°C. The mixture was allowed to stir an additional 15 minutes following the addition. The cold trifluoroacetic acid thus prepared was added dropwise to a stirred mixture of compound (XI), 5.0 grams, 0.0114 mole, finely divided anhydrous sodium carbonate, 9.5 grams, 0.089 mole, and 100 ml. of methylene chloride. The reaction mixture was allowed to reflux due to exotherm while the addition was carried out over the period of one hour. The carbonate was removed by filtration and the filtrate was treated with an additional 9.5 grams of sodium carbonate at 25°C for 15 minutes. The crude epoxide was recovered and molecular distillation produced 3.5 grams (70 percent), of pale yellow oil, boiling point 163-168°C/10⁻³ torr.

Analyses Calculated for $C_{24}H_{36}O_4Si_3$: C, 61.02%; H, 7.63%; Si, 17.80%. Found: C, 60.1%; H, 7.40%; Si, 17.90%.

Calculated epoxide equivalent weight: 236. Found: 245.

Preparation of 1,5-Bis(p-(2,3-epoxypropyl)phenyl)octamethyltetrasiloxane (XIX)

The preparation of compound (XIX) followed the general procedure described for compound (XVIII). The reactant proportions utilized were the following: Compound (XII), 5 grams, 0.0097 mole; hydrogen peroxide, 1.48 grams, 0.0389 mole; trifluoroacetic anhydride, 10.06 grams, 0.0479 mole; and sodium carbonate, 7.62 grams, 0.0719 mole. Purification by molecular distillation yielded 3.9 grams (78 percent) of pale yellow oil, boiling point 182-187°C/10⁻³ torr.

Analyses Calculated for C₂₆H₄₂O₅Si₄: C, 57.14%; H, 7.69%; Si, 20.51%. Found: C, 56.80%; H, 7.51%; Si, 20.94%.

Calculated epoxide equivalent: 273. Found: 281.

Preparation of 1,9-Bis(p-(2,3-epoxypropyl)phenyl)decamethylpentasiloxane (XX)

This preparation followed the general procedure described for compound (XVIII). The reactant proportions utilized were the following: Compound (XIII), 5 grams, 0.0085 mole; hydrogen peroxide, 1.29 grams, 0.0340 mole; trifluoroacetic anhydride, 8.80 grams, 0.0419 mole; sodium carbonate, 6.65 grams, 0.0628 mole. Purification by molecular distillation yielded 4.1 grams (82 percent) of a pale yellow oil, boiling point 191-196°C/10⁻³ torr.

Analyses Calculated for C₂₈H₄₈O₆Si₅: C, 54.19%; H, 7.74%; Si, 22.58%. Found: C, 53.50%; H, 7.05%; Si, 23.20%.

Calculated epoxide equivalent weight: 310. Found: 319.

Preparation of Tris(p-(2,3-epoxypropyl)phenyldimethylsiloxy)methylsilane (XXI)

The preparation of compound (XXI) followed the general procedure described for compound (XVIII). The stoichiometric proportions of reactants utilized to prepare compound (XXI) consisted of compound (XIV), 5 grams, 0.0075 mole; hydrogen peroxide, 1.53 grams, 0.045 mole; trifluoroacetic anhydride, 11.22 grams, 0.055 mole; sodium carbonate, 9.21 grams, 0.087 mole. The crude epoxide was purified by molecular distillation to yield 3.4 grams (68 percent) of pale yellow oil, boiling point 201-206°C/10⁻⁴ torr.

Analyses Calculated for C₃₄H₄₈O₆Si₄: C, 61.44%; H, 7.23%; Si, 16.87%. Found: C, 60.80%; H, 7.59%; Si, 17.10%.

Calculated epoxide equivalent weight: 332. Found: 339.

Preparation of 1,4-Bis((p-(2,3-epoxypropyl)phenyldimethylsiloxy)dimethylsilyl)-benzene (XXII)

Compound (XXII) was prepared by the general procedure described for preparation of compound (XVIII). The reactant proportions utilized to prepare compound (XXII) consisted of compound (XV), 5 grams, 0.00825 mole; hydrogen peroxide, 1.12 grams, 0.033 mole; trifluoroacetic anhydride, 8.21 grams, 0.041 mole; sodium carbonate, 6.89 grams, 0.065 mole. Compound (XXII) was purified by molecular distillation to yield 3.7 grams (74 percent) of pale yellow oil, boiling point 187-192°C/10⁻⁴ torr.

Analyses Calculated for C₃₂H₄₆O₄Si₄: C, 63.37%; H, 7.59%; Si, 18.48%. Found: C, 64.1%; H, 7.40%; Si, 19.96%.

Calculated epoxide equivalent weight: 303. Found: 308.

Preparation of 1,4-Bis((epoxyethyl)dimethylsiloxy)dimethylsilyl)benzene (XXIII)

Hydrogen peroxide, 89.5 percent, 1.76 grams, 0.0519 mole, was treated with trifluoroacetic anhydride, 10.83 grams, 0.0516 mole, under conditions previously described. The cold peracid thus prepared was added dropwise to a stirred mixture of compound (XVI), 5 grams, 0.0117 mole; anhydrous potassium carbonate, 8.1 grams, 0.0585 mole; and 100 ml. of methylene chloride, which was maintained at 5°C. The peracid addition was carried out over a period of 1/2-hour, after which the mixture was quickly filtered and the filtrate was treated with an additional 8.1 grams of potassium carbonate. The mixture was allowed to warm to 25°C and the carbonate treatment was discontinued when the supernatant liquid gave a neutral reaction to pH paper. The residue was fractionally distilled to give 4.3 grams (86 percent) of colorless oil, boiling point 125-127°C/5x10⁻² torr.

Analyses Calculated for C₁₈H₃₄O₄Si₄: C, 50.70%; H, 7.98%; Si, 26.29%. Found: C, 52.00%; H, 7.90%; Si, 26.60%.

Calculated epoxide equivalent weight: 213. Found: 218.

Preparation of 1,4-Bis((3,4-epoxybutyl)dimethylsiloxy)dimethylsilyl)benzene (XXIV)

A freshly distilled sample of 1,4-bis(dimethylsiloxy)dimethylsilyl)benzene (XVII), 13.8 grams, 0.0403 mole, was added dropwise to a stirred mixture of freshly distilled excess 3,4-epoxy-1-butene and one ml. of chloroplatinic acid in acetone. The catalyst solution was prepared by dissolving 0.01 gram of chloroplatinic acid in 10 ml. of acetone. The reaction mixture was stirred at 70-75°C under nitrogen throughout the addition period of 1-1/2 hours. Following the addition, the mixture was treated with 0.5 ml. of catalyst solution and stirred for an

additional 1/2-hour at 70-75°C. It was then stirred at room temperature overnight. The mixture was dissolved in 50 ml. of methylene chloride, and treated successively with 0.1 gram of sodium bicarbonate, and filtered through basic alumina. The product was recovered by fractional distillation in 70 percent yield as a colorless oil, boiling point 137-140°C/5x10⁻³ torr.

Analyses Calculated for C₂₂H₄₂O₄Si₄: C, 54.77%; H, 8.71%; Si, 23.24%. Found: C, 53.80%; H, 8.41%; Si, 23.54%.

Calculated epoxide equivalent weight: 241. Found: 248.

Preparation of Bis(p-aminophenoxy)dimethylsilane (XXV)

Bis(dimethylamino)dimethylsilane (IV), 10 grams, 0.0685 mole, was added dropwise to a refluxing solution of freshly sublimed p-aminophenol, 14.93 grams, 0.137 mole, in benzene. The reaction mixture was heated at benzene reflux for one-hour following the addition. The crude product was recrystallized from benzene/petroleum ether in 60 percent yield, as amber crystals, melting point 62-63°C, literature melting point 63°C (ref. 6).

Analyses Calculated for C₁₄H₁₈N₂O₂Si: C, 46.03%; H, 6.57%; N, 10.22%; Si, 10.22%. Found: C, 45.22%; H, 6.65%; N, 10.05%; Si, 10.95%.

Preparation of 1,3-Bis(p-aminophenoxy)tetramethyldisiloxane (XXVI)

1,3-Bis(dimethylamino)tetramethyldisiloxane (V), 10 grams, 0.045 mole, was added to p-aminophenol 9.9 grams, 0.0908 mole, following the procedure outlined for compound (XXV). The crude product distilled as an amber oil at 175-180°C/0.18 torr.

Analyses Calculated for C₁₆H₂₄N₂O₃Si₂: C, 55.17%; H, 6.89%; N, 8.04%; Si, 16.09%. Found: C, 54.44%; H, 6.21%; N, 7.49%; Si, 16.32%.

Preparation of 1,5-Bis(p-aminophenoxy)hexamethyltrisiloxane (XXVII)

1,5-Bis(dimethylamino)hexamethyltrisiloxane (VI), 10 grams, 0.0226 mole, was added to p-aminophenol, 4.93 grams, 0.0452 mole, following the procedure outlined for compound (XXV). The crude product distilled as an amber oil at 215-220°C/0.2 torr.

Analyses Calculated for C₁₈H₃₀N₂O₄Si₃: C, 48.87%; H, 6.79%; Si, 19.00%; N, 6.33%. Found: C, 47.90%; H, 6.92%; Si, 19.25%; N, 6.21%.

CONCLUSIONS

Polymers having a wide range of electrical properties and mechanical toughness were obtained through various combinations of the intermediates in Table I. A trend toward lower dielectric constants to a minimum of 3.1 was observed with successively longer blocks of the siloxane moiety, with some sacrifice in mechanical strength or toughness. The trifunctional epoxide (XXI) would be appropriate for applications requiring high modulus embedments whereas the highly flexible diepoxide (XX) would provide a lower strength, flexible embedment. Compound (XXII), having both the silphenylene and siloxane linkages, resulted in a polymer with the best balance of properties with a dielectric constant of 3.2 and a high degree of mechanical toughness. Formulations 1, 2, 3, and 5, listed in Table I, were qualitatively determined by flexing to be stiff but non-brittle at -50°C .

The effects of increasing the length of the siloxane blocks within the diamine crosslinking agents apparently resulted in a downward trend in dielectric constant as indicated in Table II for formulations 1, 9, and 10; however, this trend should be considered only in a general sense due to the relatively small changes observed in the dielectric constants.

In view of the promising dielectric properties and processability of this series of polymers as embedment materials, further efforts will be expended to prepare large quantities of selected intermediates, principally (XVIII), (XIX), (XX), (XXI), and (XXII), to allow detailed evaluation of the electrical, mechanical, and thermal properties of polymers produced from these intermediates.

APPENDIX A
INFRARED SPECTRA

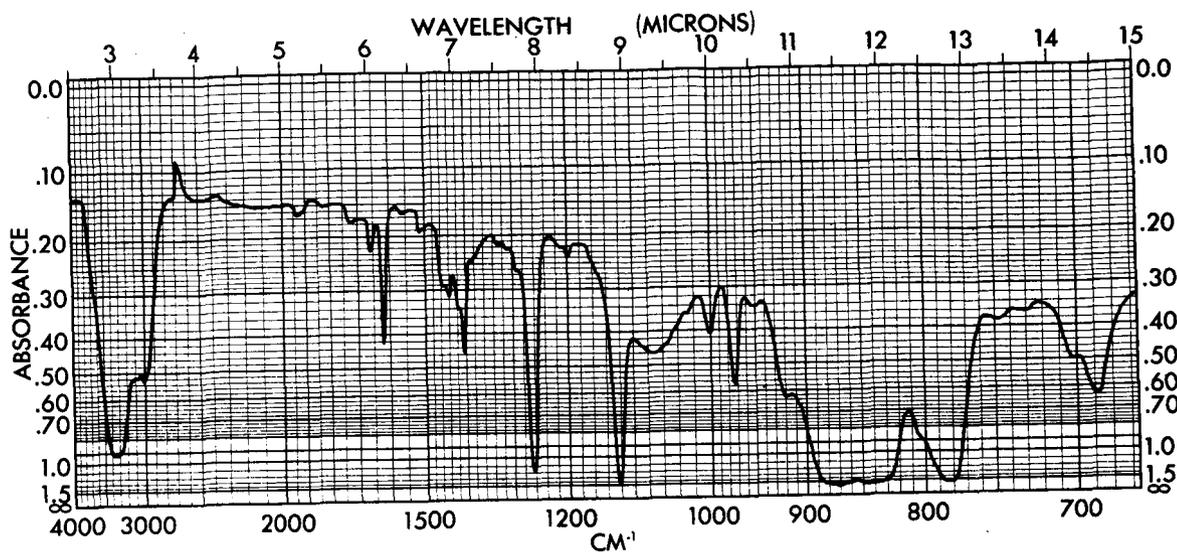


FIGURE 1.- INFRARED SPECTRUM OF *p*-ALLYLPHENYLDIMETHYLSILANOL (II)

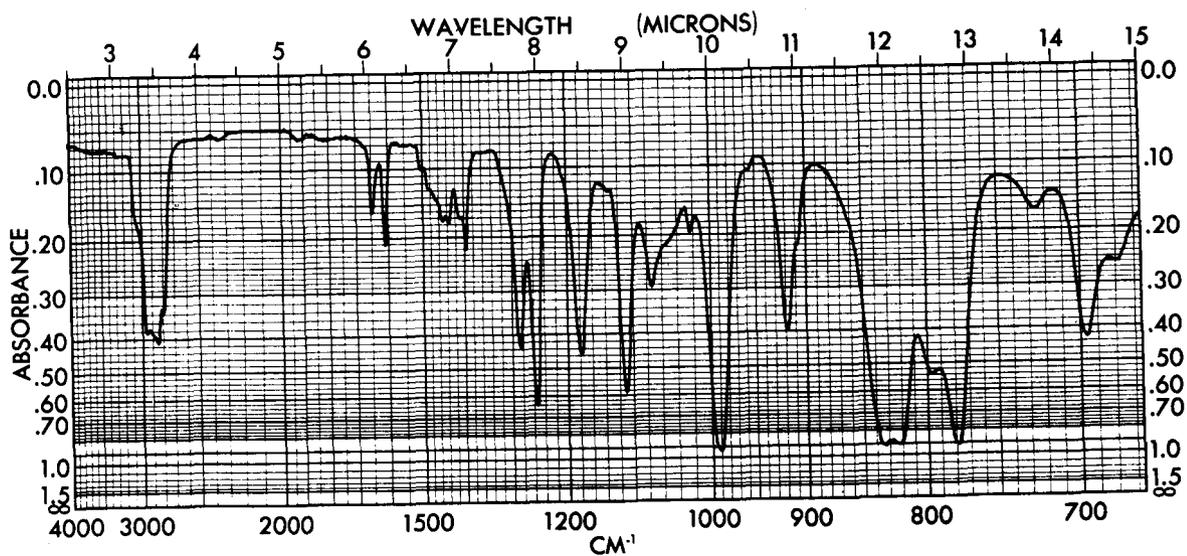


FIGURE 2.- INFRARED SPECTRUM OF
p-ALLYLPHENYL-N,N-DIMETHYLAMINODIMETHYLSILANE (III).

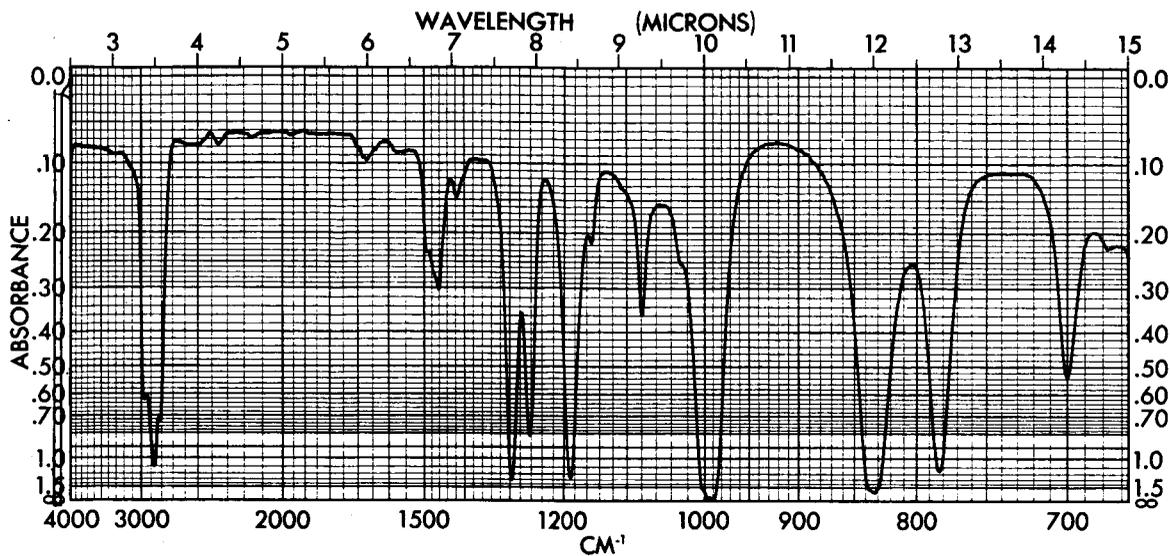


FIGURE 3.- INFRARED SPECTRUM OF BIS(DIMETHYLAMINO)DIMETHYLSILANE (IV).

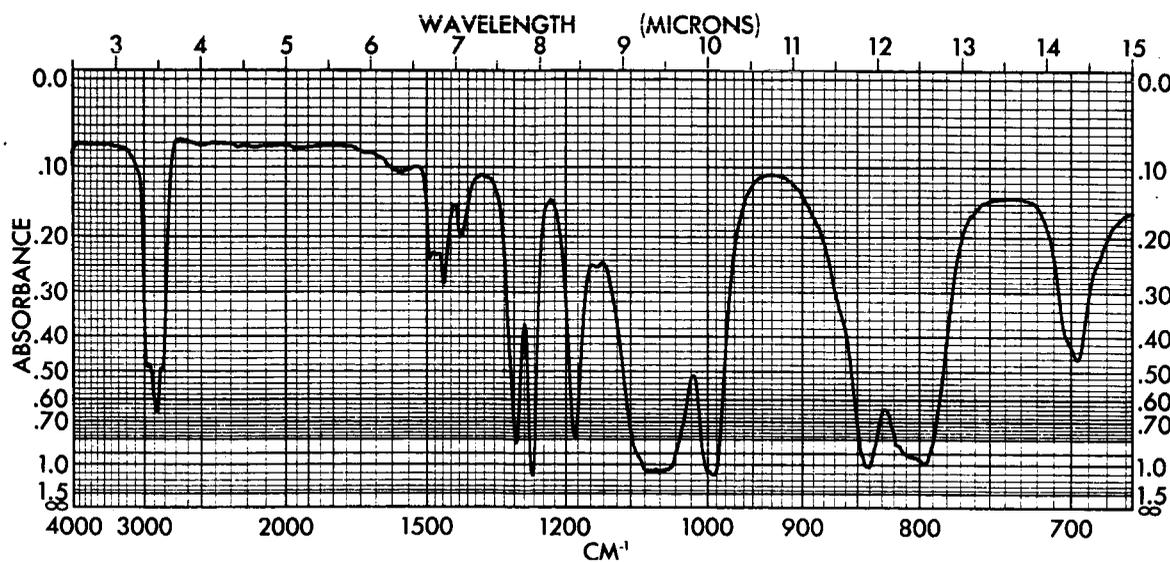


FIGURE 4.- INFRARED SPECTRUM OF
1,3-BIS(DIMETHYLAMINO)TETRAMETHYLDISILOXANE (V).

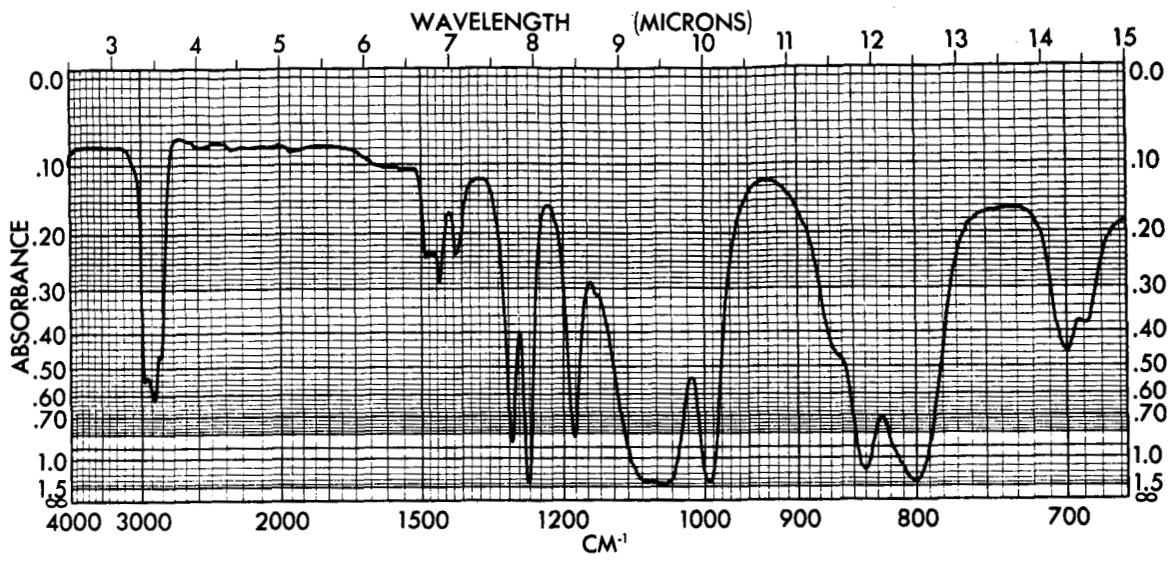


FIGURE 5.- INFRARED SPECTRUM OF
1,5-BIS(DIMETHYLAMINO)HEXAMETHYLTRISILOXANE (VI).

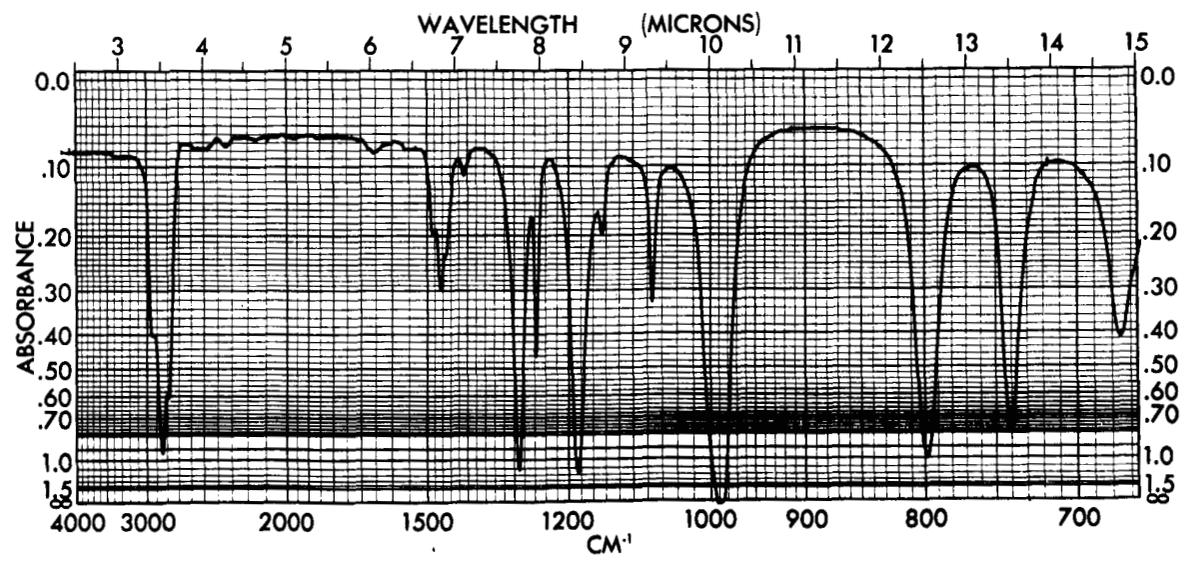


FIGURE 6.- INFRARED SPECTRUM OF METHYL-TRIS(DIMETHYLAMINO)SILANE (VII).

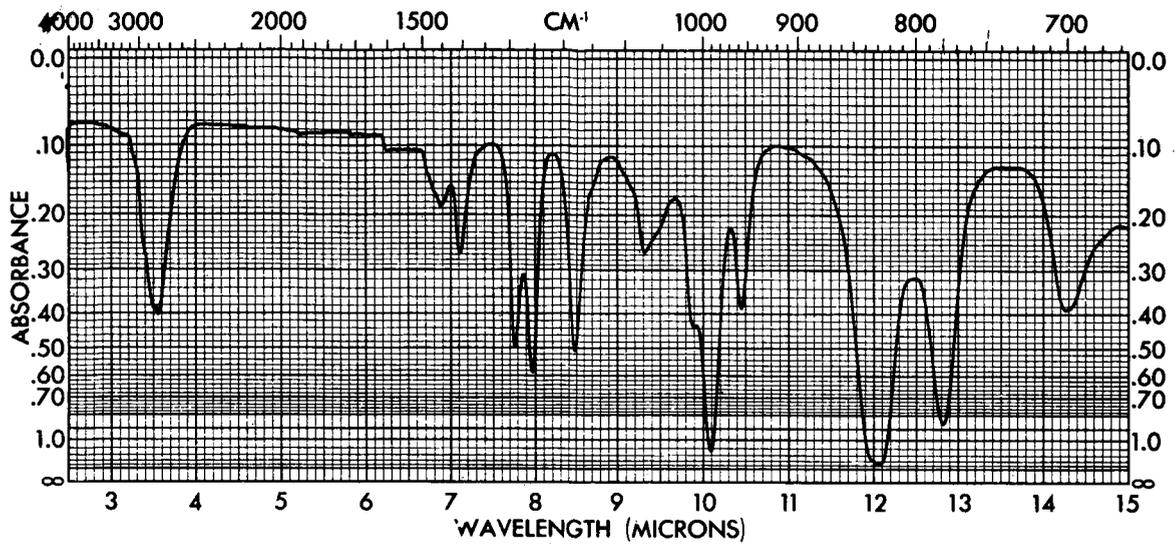


FIGURE 7.- INFRARED SPECTRUM OF
VINYL DIMETHYL-N,N-DIMETHYLAMINOSILANE (VIII).

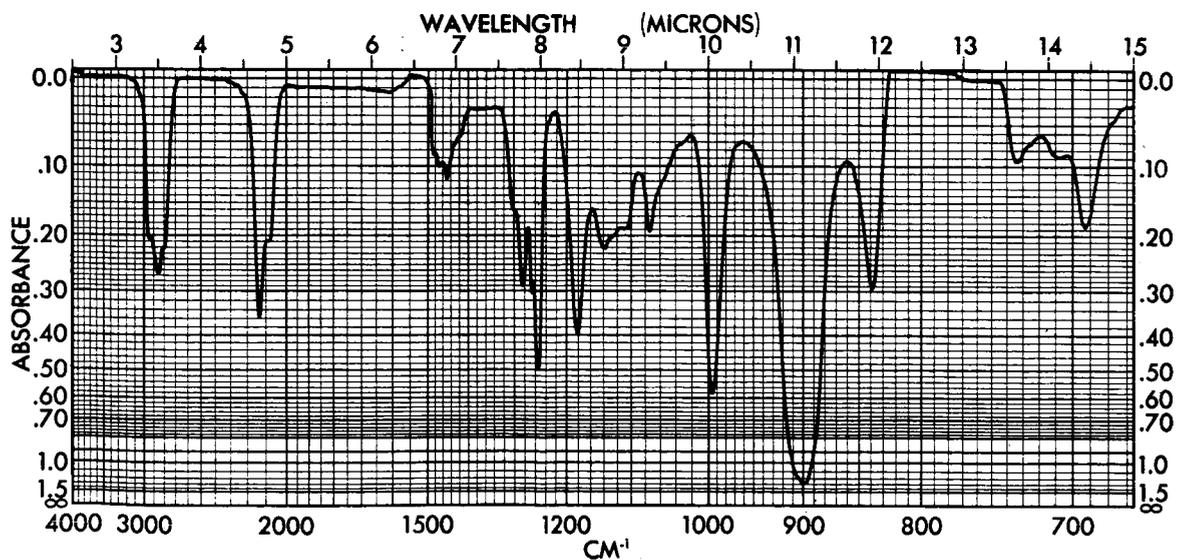


FIGURE 8.- INFRARED SPECTRUM OF DIMETHYL-N,N-DIMETHYLAMINOSILANE (IX).

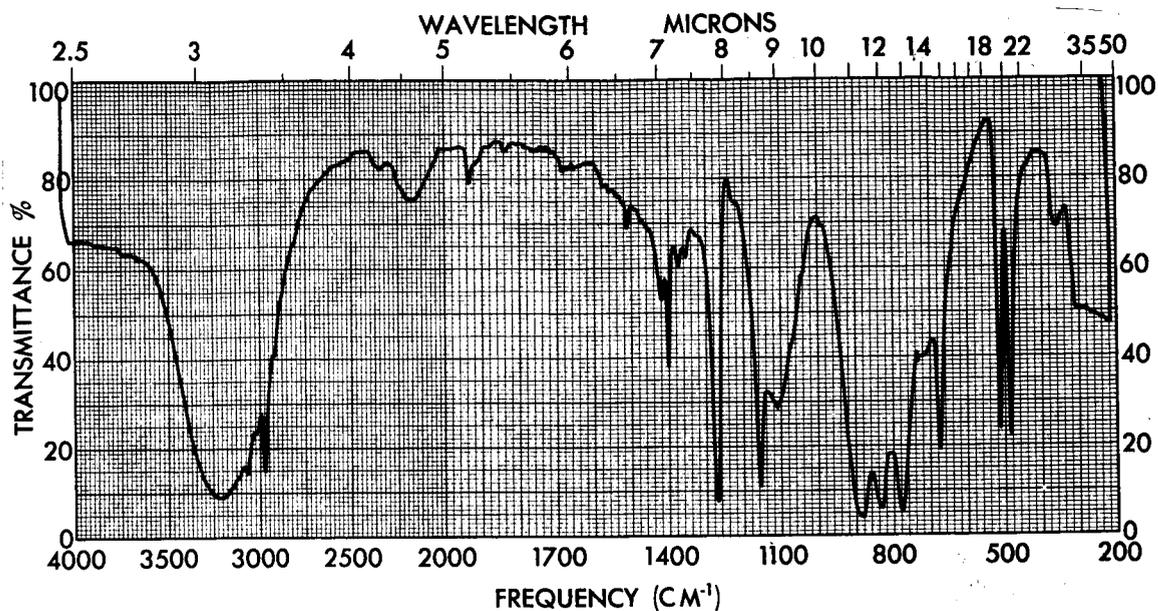


FIGURE 9.- INFRARED SPECTRUM OF 1,4-BIS(HYDROXYDIMETHYLSILYL)BENZENE (X).

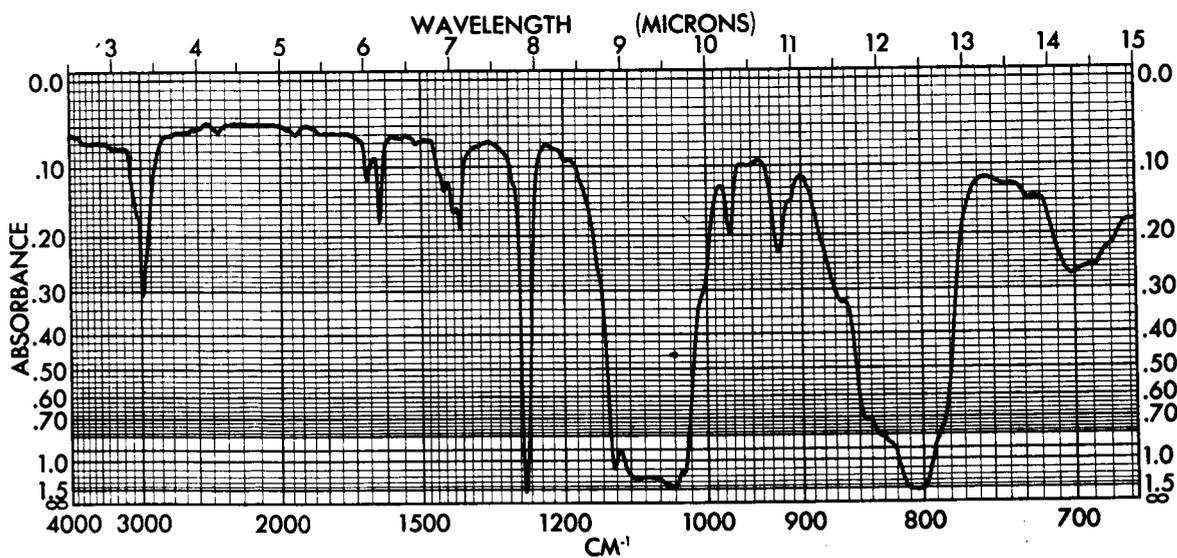


FIGURE 10.- INFRARED SPECTRUM OF
1,5-BIS(p-ALLYLPHENYL)-HEXAMETHYLTRISILOXANE (XI).

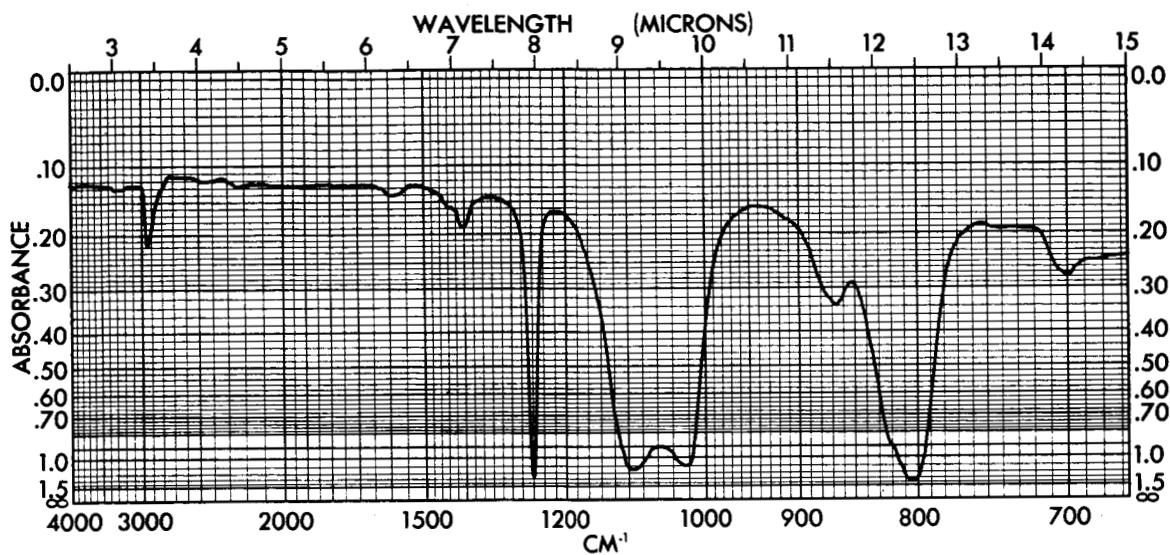


FIGURE 11.- INFRARED SPECTRUM OF
1,7-BIS(*p*-ALLYLPHENYL)OCTAMETHYLTETRASILOXANE (XII).

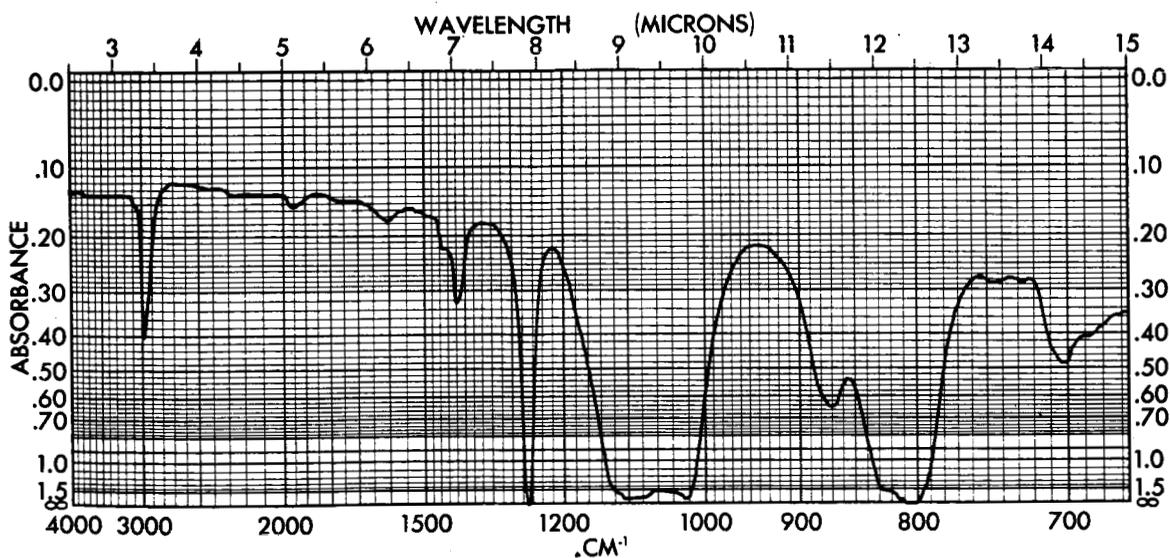


FIGURE 12.- INFRARED SPECTRUM OF
1,9-BIS(*p*-ALLYLPHENYL)DECAMETHYLPENTASILOXANE (XIII).

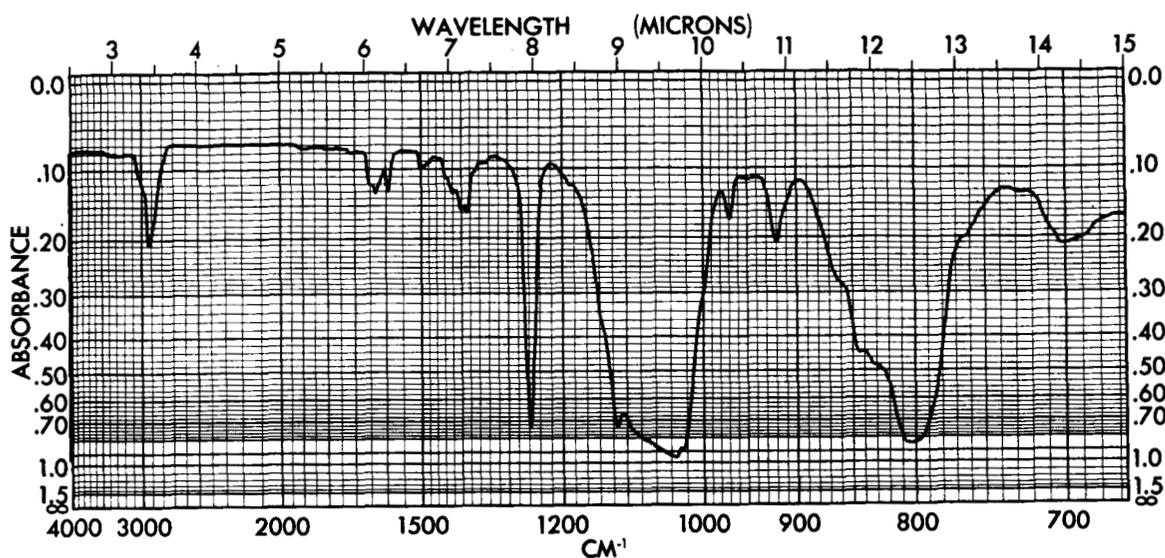


FIGURE 13.- INFRARED SPECTRUM OF
METHYL-TRIS(p-ALLYLPHENYLDIMETHYLSILOXY)SILANE (XIV).

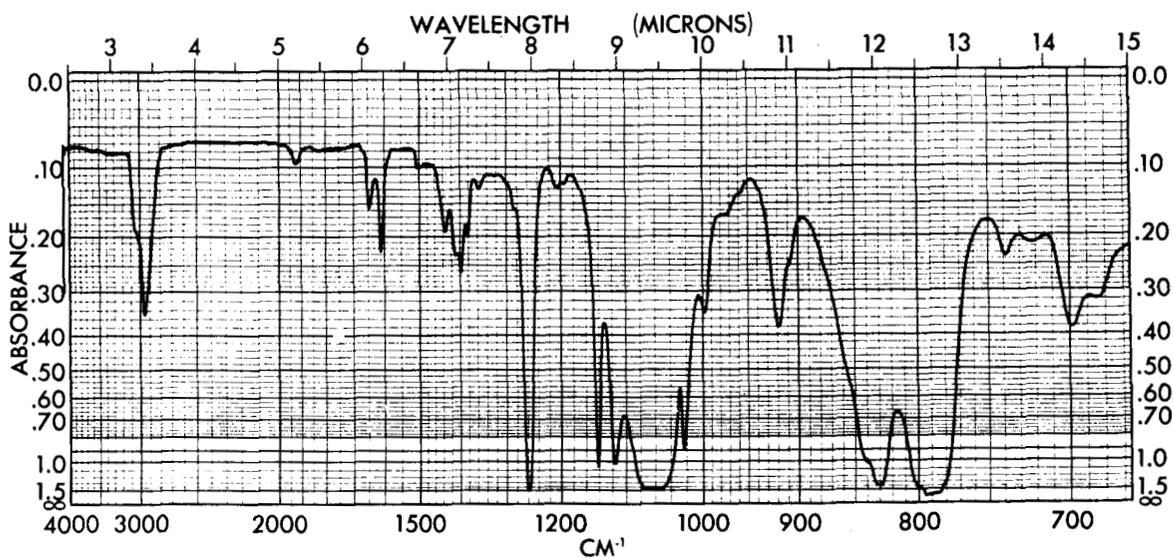


FIGURE 14.- INFRARED SPECTRUM OF
1,4-BIS [(p-ALLYLPHENYLDIMETHYLSILOXY)DIMETHYLSILYL]BENZENE (XV).

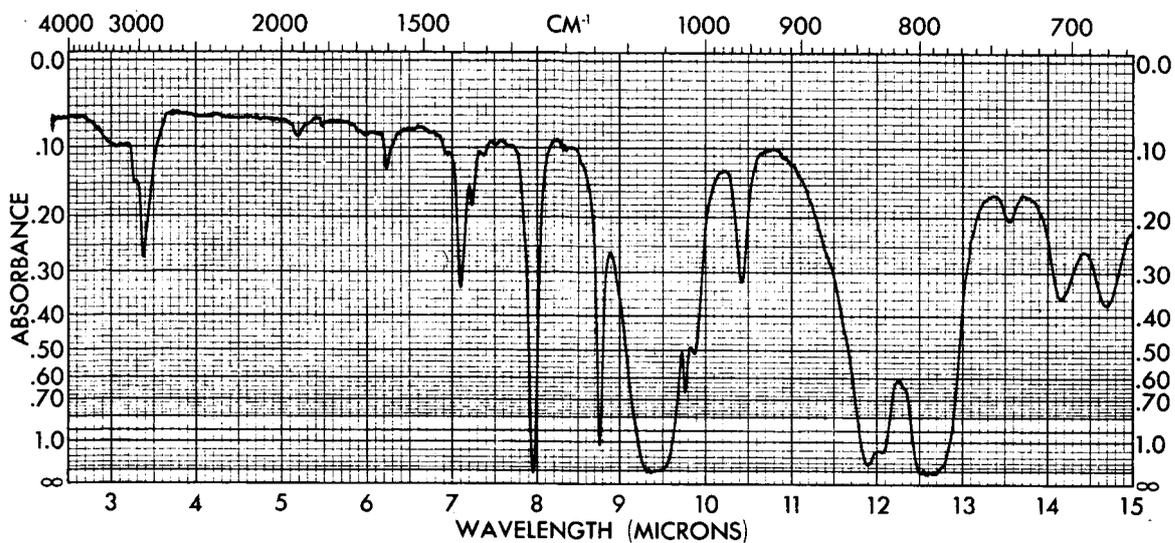


FIGURE 15.- INFRARED SPECTRUM OF
 1,4-BIS [(VINYLDIMETHYLSILOXY)DIMETHYLSILYL] BENZENE (XVI).

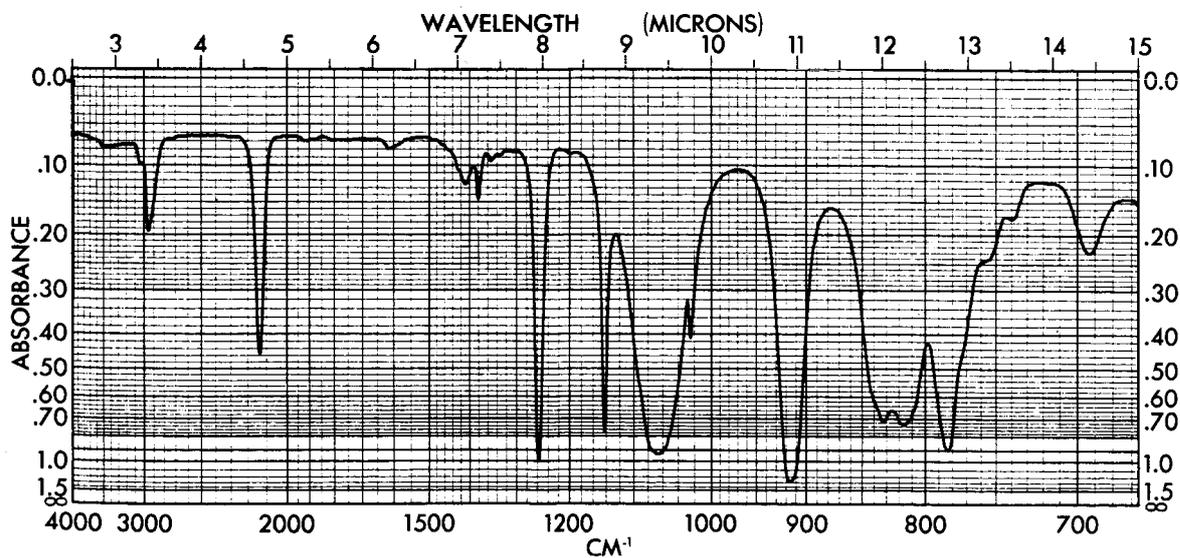


FIGURE 16.- INFRARED SPECTRUM OF
 1,4-BIS [(DIMETHYLSILOXY)DIMETHYLSILYL] BENZENE (XVII).

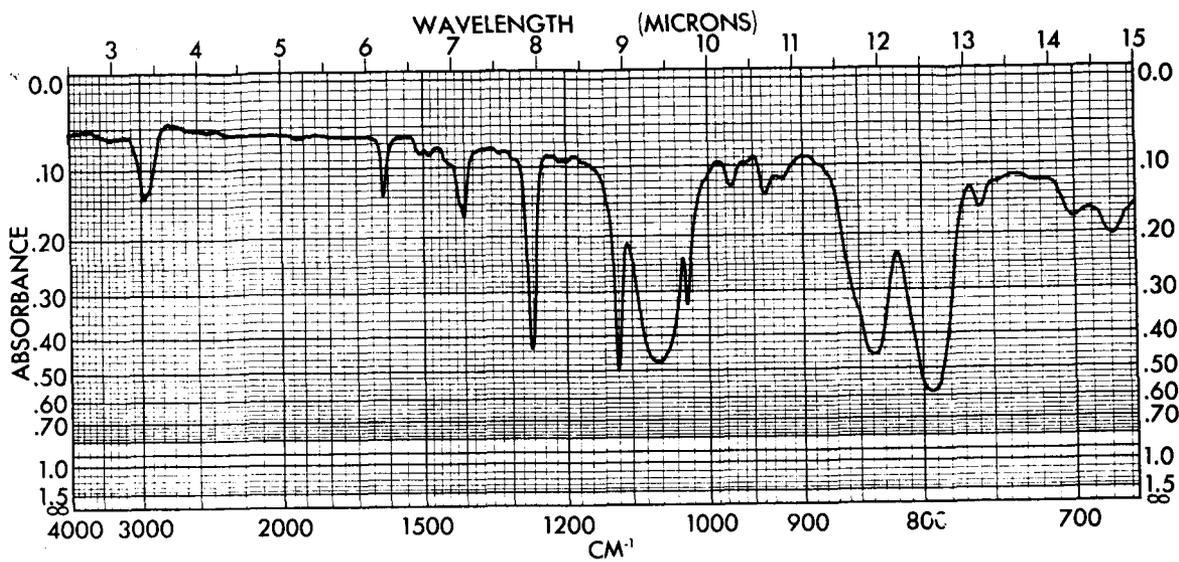


FIGURE 17.- INFRARED SPECTRUM OF
1,5-BIS(p-(2,3-EPOXYPROPYL)PHENYL)HEXAMETHYLTRISILOXANE (XVIII).

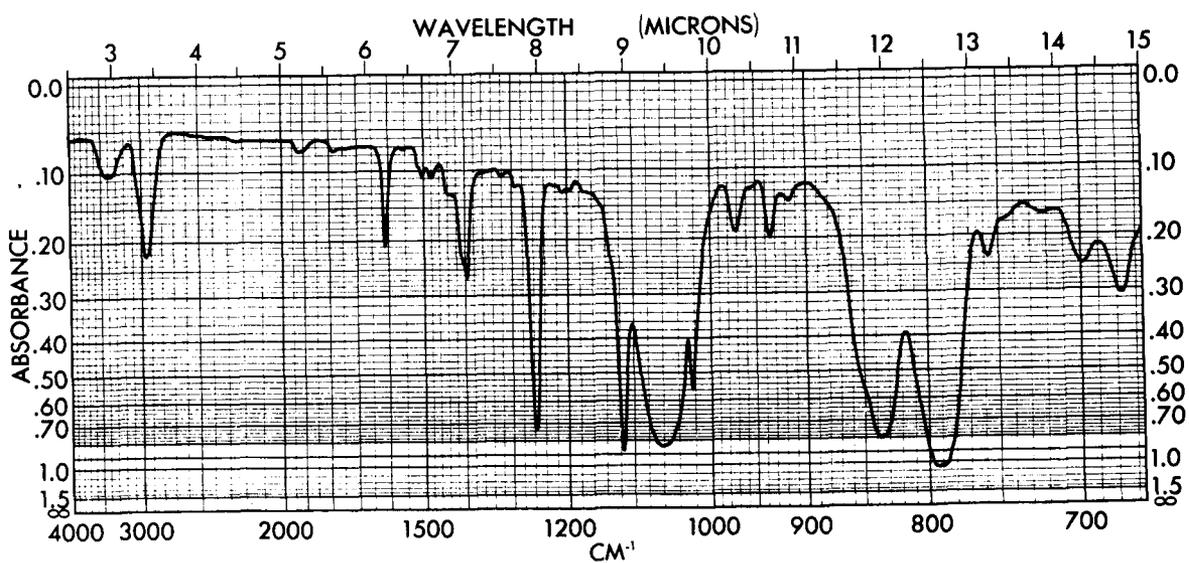


FIGURE 18.- INFRARED SPECTRUM OF
1,7-BIS(p-(2,3-EPOXYPROPYL)PHENYL)OCTAMETHYLTETRSILOXANE (XIX).

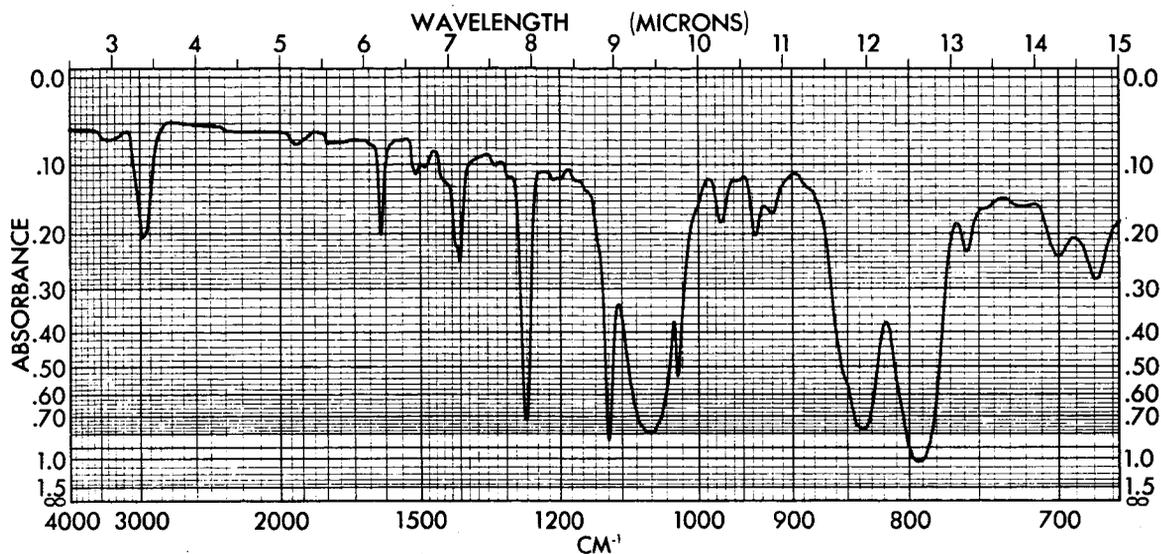


FIGURE 19.- INFRARED SPECTRUM OF
1,9-BIS(p-(2,3-EPOXYPROPYL)PHENYL)DECAMETHYLPENTASILOXANE (XX).

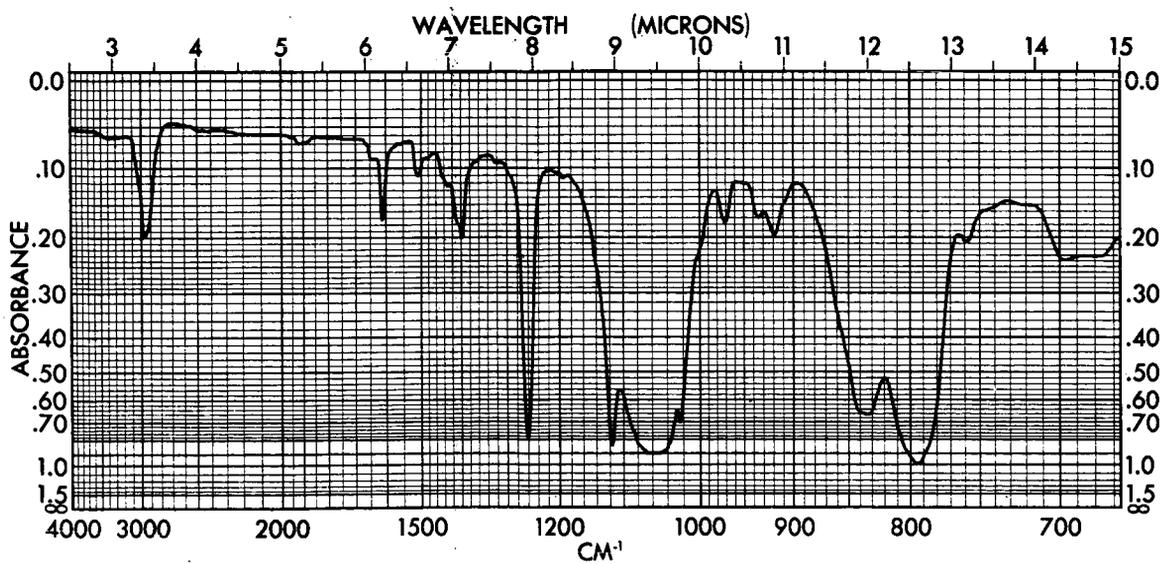


FIGURE 20.- INFRARED SPECTRUM OF
METHYLTRIS(p-(2,3-EPOXYPROPYL)PHENYLDIMETHYLSILOXY)SILANE (XXI).

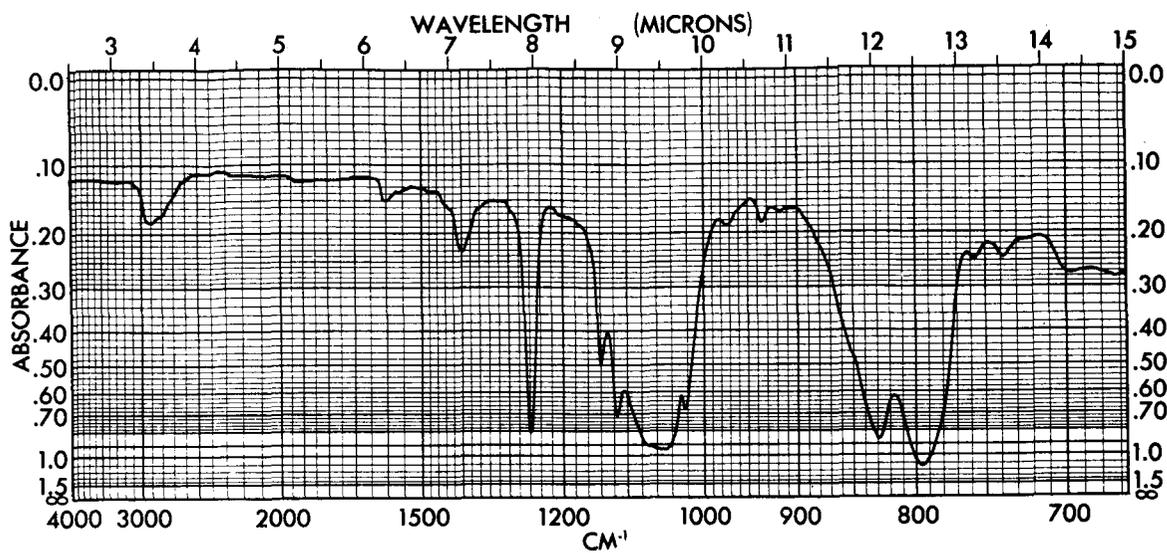


FIGURE 21.- INFRARED SPECTRUM OF
1,4-BIS((*p*-(2,3-EPOXYPROPYL)PHENYL)DIMETHYLSILOXY)DIMETHYLSILYL)BENZENE (XXII).

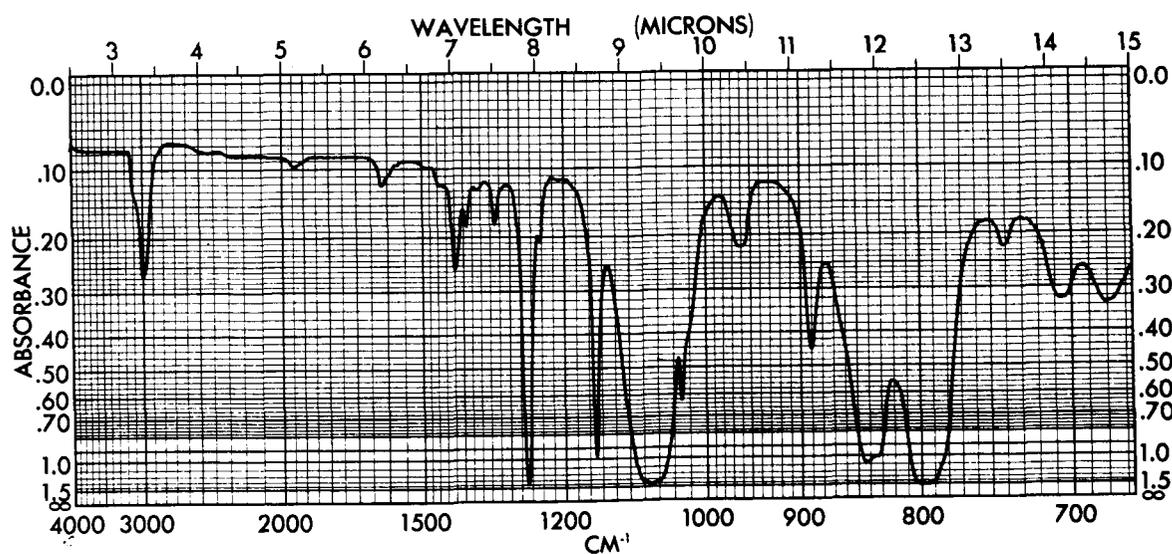


FIGURE 22.- INFRARED SPECTRUM OF
1,4-BIS((EPOXYETHYL)DIMETHYLSILOXY)DIMETHYLSILYL)BENZENE (XXIII).

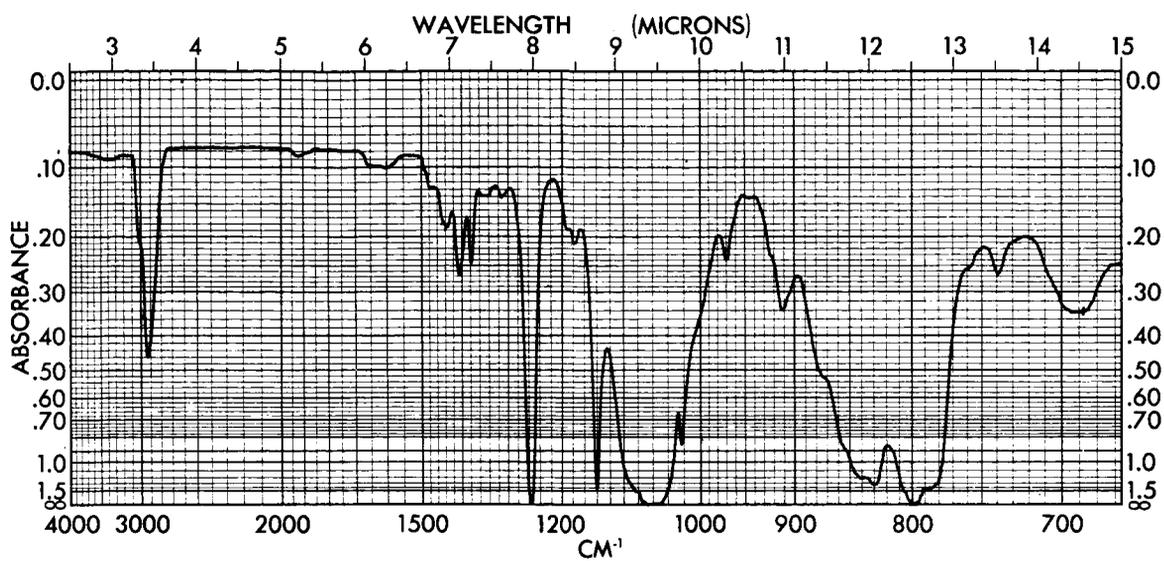


FIGURE 23.- INFRARED SPECTRUM OF
1,4-BIS((3,4-EPOXYBUTYLDIMETHYLSILOXY)DIMETHYLSILYL)BENZENE (XXIV).

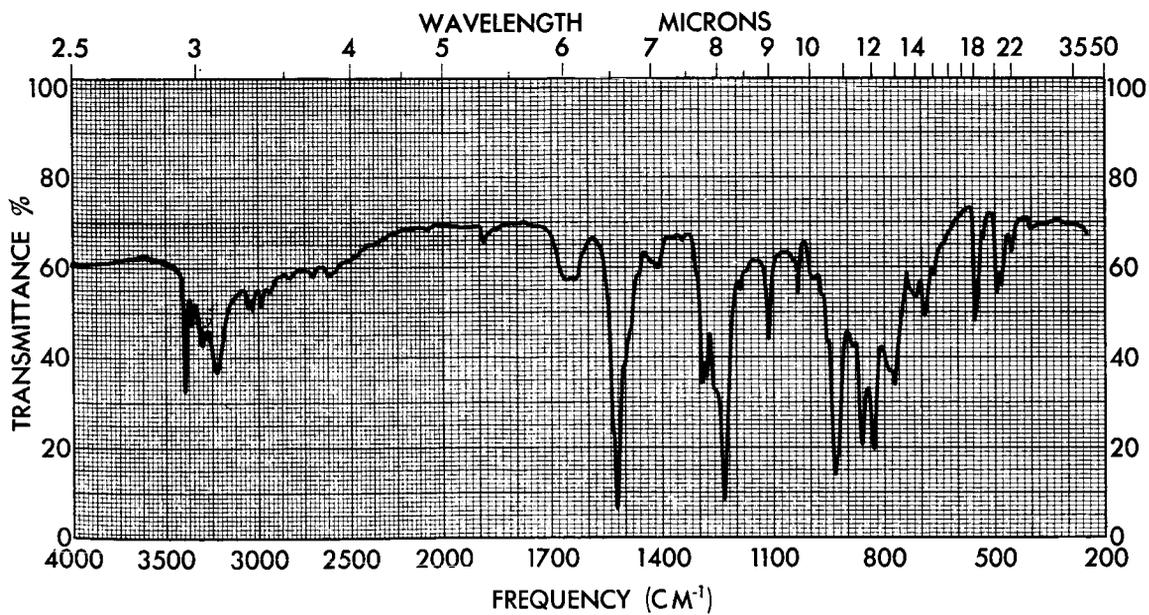


FIGURE 24.- INFRARED SPECTRUM OF BIS(p-AMINOPHENOXY)DIMETHYLSILANE (XXV).

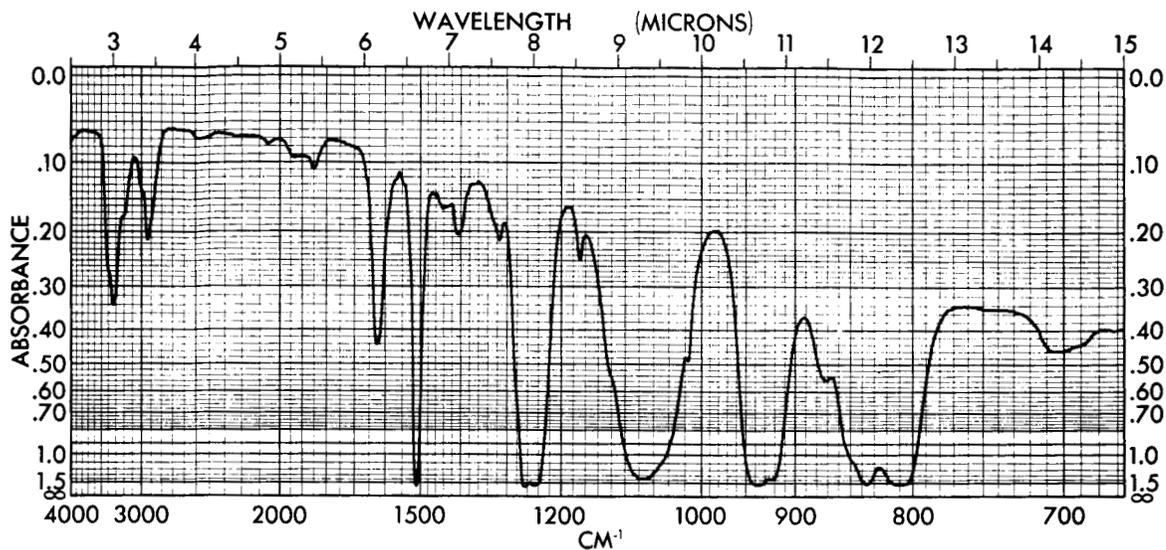


FIGURE 25.- INFRARED SPECTRUM OF
1,3-BIS(p-AMINOPHENOXY)TETRAMETHYLDISILOXANE (XXVI).

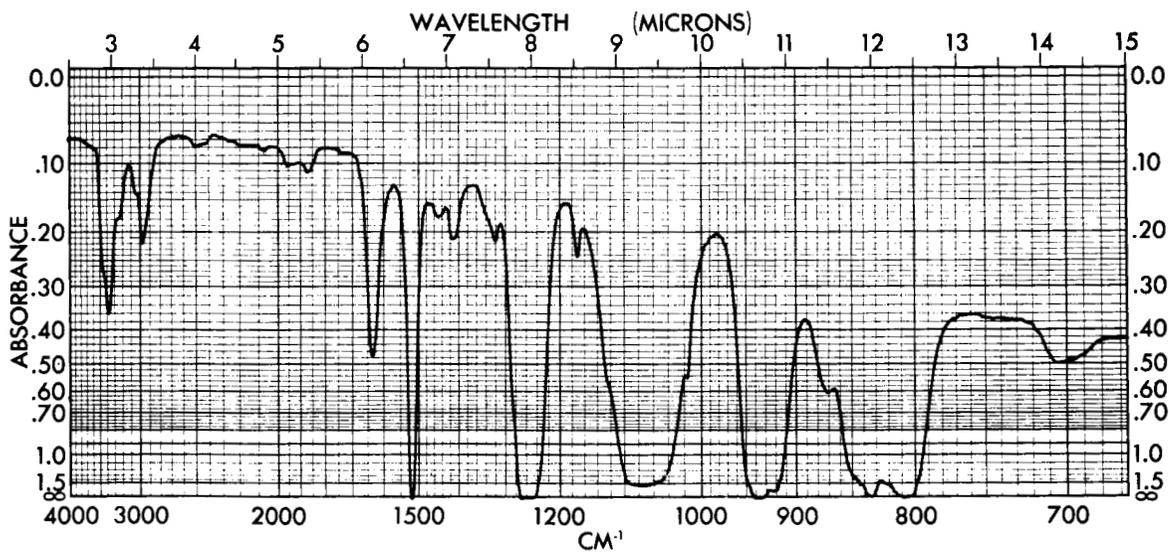


FIGURE 26.- INFRARED SPECTRUM OF
1,5-BIS(p-AMINOPHENOXY)HEXAMETHYLTRISILOXANE (XXVII).

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January 26, 1968

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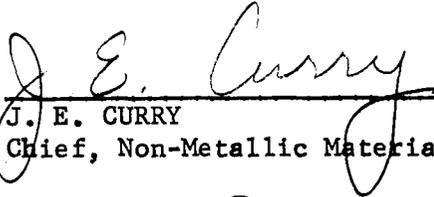
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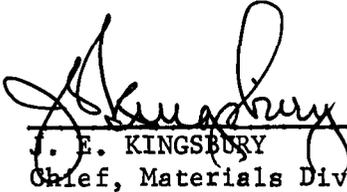
by William J. Patterson

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